



***Quantifying Spatial and Temporal Deposition of  
Atmospheric Pollutants in Runoff from Different Pavement  
Types***

*A thesis submitted in partial fulfilment of the requirements for the  
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*“When you put your hand in a flowing stream, you touch the last that has gone before and the first of what is still to come”*

- *Leonardo da Vinci*

## ABSTRACT

Urban development leads to increased impermeable landscapes that interrupt the hydrological cycle by creating an impermeable barrier to the natural infiltration of precipitation. Precipitate, unable to infiltrate, flows over impermeable surfaces as sheet runoff, carrying the pollutants from the land with it; thus comprising the quality of the stormwater. The runoff is redirected (frequently untreated) to nearby waterways altering their water quality and quantity, thereby, adversely affecting receiving aquatic ecosystems. Suspended solids and elevated heavy metal concentrations in stormwater are the leading causes of water quality degradation in urban waterways in New Zealand. It is widely reported that vehicles and metal roofs are a major *direct* source of the key pollutants (total suspended solids (TSS) and heavy metals) in stormwater runoff; however, the contribution of atmospheric deposition, as an *indirect* source, in stormwater runoff is rarely considered. This is principally due to the many uncertainties and challenges with measuring and managing these pollutants in stormwater runoff. Therefore, a monitoring programme into the dynamics controlling atmospherically derived pollutant build-up and wash-off from urban surfaces was conducted. In particular, this research focused on the spatial and temporal variability of Cu, Zn, Pb, and TSS deposition in different land-use areas; the influence of pavement type on atmospherically-deposited pollutant loads in stormwater; and the contribution of wet deposition and dry deposition to the total deposition loads.

Impermeable concrete boards ( $\approx 1 \text{ m}^2$ ) were deployed for 11 months in different land-use areas (industrial, residential and airside) in Christchurch, New Zealand, to capture spatially distributed atmospheric deposition loads in runoff over varying meteorological conditions. Mixed-effect regression models were developed to explain the influence of different meteorological characteristics on pollutant build-up and wash-off dynamics. Next, impermeable asphalt, permeable asphalt, impermeable concrete, and permeable concrete boards were deployed for two months in a residential land-use area to determine the influence of pavement composition and roughness on pollutant loads in stormwater. Finally, wet deposition samples were analysed in an industrial land-use area for 8 months to monitor the

contribution of wet deposition to atmospherically-deposited pollutant loads. All samples were analysed for total and dissolved Cu, Zn, Pb, and TSS.

*Pavement type:* Results showed that both impermeable and permeable concrete were efficient at retaining Cu and Zn. Bitumen leaching from the impermeable asphalt was a significant source of Zn to runoff. However, bitumen leaching from the permeable asphalt did not contain elevated Zn loads. Infiltrate from the permeable asphalt provided little/no removal of Cu and Zn. Impermeable asphalt provided greater retention of TSS and Pb over impermeable concrete because its rougher surface entrapped more particulates. TSS and Pb loads were the lowest from the permeable pavements due to the pavers filtering out particulates.

*Spatial variability:* Results showed that all three land-use areas exhibited similar patterns of varying metal and TSS loads, indicating that atmospherically-deposited metals and TSS had a homogenous distribution within the Christchurch airshed. This suggested that the pollutants originated from a similar source and that the surrounding land-use was not an important factor in determining atmospheric pollutant loads to stormwater runoff. Although, higher pollutant loads were found for the industrial area, this was attributed to local topographic conditions rather than land-use activity.

*Temporal variability:* Results illustrated the importance of antecedent dry days on pollutant build-up. Peak rainfall intensity and rain duration had a significant relationship with TSS and Pb wash-off; rain depth had a significant relationship with Cu and Zn wash-off. This suggested that the pollutant speciation phase plays an important role in surface wash-off. Rain intensity and duration influenced particulate pollutants, whereas, rain depth influenced dissolved pollutants. Additionally, mixed-effect models could predict approximately 53-69% of the variation in airborne pollutant loads in runoff.

*Deposition pathways:* Wet deposition was an important contributor of dissolved Zn to stormwater runoff. However, dry deposition was the greatest source of total Cu, Zn, and Pb loads in stormwater runoff. This is principally due to the low annual rainfall in Christchurch

limiting pollutant removal via wet deposition unlike dry deposition, which is continually occurring.

Understanding the dynamics of airborne pollutant deposition and their contribution to stormwater pollution could help stormwater managers in strategic decision-making processes such as choice of location and installation of different treatment systems.

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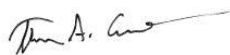
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# TABLE OF CONTENTS

<b>ABSTRACT .....</b>	<b>iii</b>
<b>ACKNOWLEDGMENTS .....</b>	<b>viii</b>
<b>TABLE OF FIGURES.....</b>	<b>xv</b>
<b>TABLE OF TABLES.....</b>	<b>xviii</b>
<b>GLOSSARY OF TERMS.....</b>	<b>xxi</b>
<b>RESEARCH OUTPUTS .....</b>	<b>xxiii</b>
<b>1. INTRODUCTION .....</b>	<b>2</b>
1.1. Statement of Problem .....	2
1.2. Atmospheric Pollutant Transport to Waterways .....	2
1.3. Purpose of Research .....	3
1.3.1. Scope of objectives .....	4
1.4. Scope of Thesis.....	5
<b>2. BACKGROUND .....</b>	<b>7</b>
2.1. Urban Stormwater Runoff .....	7
2.1.1. Physical responses .....	7
2.1.2. Biological responses .....	9
2.1.3. Chemical responses .....	10
2.1.4. Direct sources of Cu, Pb, and Zn to stormwater runoff.....	12
2.2. Atmospheric Deposition .....	14
2.3. Regulations .....	18
2.3.1. Stormwater regulations .....	18
2.3.2. Atmospheric pollution regulations .....	19
<b>3. MATERIALS AND METHODS.....</b>	<b>21</b>
3.1. Rationale for Methodology Employed .....	21
3.2. Experimental Components .....	22
3.3. Impermeable Paving Slab System .....	23
3.3.1. Impermeable concrete boards.....	24
3.3.2. Impermeable asphalt boards .....	25

3.3.3.	Impermeable asphalt and concrete board design .....	25
3.3.4.	Dexion frame .....	28
3.3.5.	Stormwater collection system.....	28
3.4.	Permeable Paving Slab System .....	30
3.4.1.	Permeable paving slab system design .....	31
3.4.2.	Stormwater collection system.....	32
3.5.	Surface Roughness Properties of the Pavement Types .....	33
3.6.	Background pollution from the pavement boards .....	34
3.7.	Sample Locations .....	35
3.8.	Sampling Procedure.....	39
3.8.1.	Weather data .....	40
3.8.2.	Comparison with past weather conditions.....	41
3.8.3.	PM monitoring.....	42
3.8.4.	Wet deposition sampling .....	43
3.8.5.	Bulk deposition sampling .....	44
3.9.	Analytical Analysis .....	44
3.9.1.	pH .....	46
3.9.2.	Alkalinity .....	46
3.9.3.	Specific conductivity .....	47
3.9.4.	Turbidity and total suspended solids .....	47
3.9.5.	Heavy metals .....	47
3.9.6.	Quality control and quality assurance .....	48
3.10.	Statistical Analysis .....	49
3.10.1.	MANOVA and effect-size analyses .....	49
3.10.2.	Bivariate correlation .....	50
3.10.3.	Mixed effect modelling.....	50
3.10.4.	Principle component analysis .....	51
<b>4.</b>	<b>THE INFLUENCE OF DIFFERENT PAVEMENT TYPES ON ATMOSPHERIC POLLUTANT ATTENUATION AND WASH-OFF .....</b>	<b>53</b>
4.1.	Introduction .....	53
4.1.1.	Asphalt pavements.....	53

4.1.2.	Concrete pavements.....	54
4.1.3.	Impermeable concrete versus impermeable asphalt roads .....	55
4.1.4.	Permeable pavements .....	56
4.1.1.	The influence of pavement composition on pollutant wash-off.....	60
4.2.	Materials and Methods Overview .....	62
4.3.	Results and Discussion .....	64
4.3.1.	Background pollution from the pavement boards .....	64
4.3.2.	Summary of rainfall events sampled .....	65
4.3.3.	Summary of pollutants loads in runoff from different pavement types .....	66
4.3.4.	Ecotoxicity of stormwater .....	78
4.3.5.	Behaviour of pavement leaching over time.....	79
4.4.	Pavement-pollution interactions from a trafficked road.....	81
4.5.	Conclusion.....	82
<b>5.</b>	<b>ATMOSPHERICALLY DERIVED POLLUTANTS IN STORMWATER RUNOFF FROM DIFFERENT LAND-USE AREAS ..</b>	<b>85</b>
5.1.	Introduction .....	85
5.2.	Materials and Methods Overview .....	87
5.3.	Results and Discussion .....	88
5.3.1.	Background pollution from the impermeable concrete boards .....	88
5.3.2.	Summary of rain events captured .....	89
5.3.3.	Summary of pollutants loads in runoff .....	89
5.3.4.	Spatial pattern of atmospherically derived pollutants in stormwater runoff .....	90
5.3.5.	Dry deposition rate .....	93
5.3.6.	Potential sources of atmospheric metals.....	96
5.4.	Conclusion.....	100
<b>6.</b>	<b>MODELLING AIRBORNE POLLUTANT LOADS IN STORMWATER RUNOFF .....</b>	<b>103</b>
6.1.	Introduction .....	103
6.1.1.	Urban stormwater quality modelling.....	103
6.1.2.	Process-based models .....	103
6.1.3.	Regression models.....	107

6.1.4.	Process-based models versus regression models.....	107
6.1.5.	Modelling airborne pollutant loads in stormwater runoff .....	112
6.2.	Materials and Methods Overview .....	113
6.2.1.	Analysis of pollutant build-up and wash-off .....	113
6.3.	Results and Discussion .....	116
6.3.1.	Summary of input data .....	116
6.3.2.	Pollutant build-up and pollutant wash-off models .....	117
6.3.3.	Regression models for predicting stormwater pollutant loads .....	118
6.3.4.	Influencing meteorological variables .....	123
6.4.	Conclusions .....	126
<b>7.</b>	<b>THE CONTRIBUTION OF PARTICULATE MATTER AND WET DEPOSITION TO TOTAL COPPER, LEAD, AND ZINC DEPOSITION</b>	<b>128</b>
7.1.	Introduction .....	128
7.1.1.	Particulate matter.....	128
7.1.2.	Wet deposition.....	131
7.2.	Materials and Methods Overview .....	132
7.3.	Results and Discussion .....	133
7.3.1.	Data summary.....	133
7.3.2.	Particulate matter with varying antecedent dry periods .....	135
7.3.3.	Particulate matter and wet deposition.....	136
7.3.4.	Wet deposition.....	137
7.3.5.	Contribution of WD to BD loads.....	138
7.4.	Conclusion.....	141
<b>8.</b>	<b>CONCLUSIONS AND RECOMMENDATIONS .....</b>	<b>143</b>
8.1.	Conclusions .....	143
8.2.	Recommendations for future work .....	146
8.2.1.	Polluting potential of asphalt.....	146
8.2.2.	Treatment performance of permeable pavements with varying pavement thickness.....	147
8.2.3.	Atmospheric pollutant wash-off from varying materials .....	147

8.2.4.	Characterising the spatial variability of atmospheric deposition patterns .....	148
8.2.5.	Characterising atmospheric deposition patterns for other airsheds .....	148
8.2.6.	Sources of atmospheric pollutants in Christchurch .....	148
8.2.7.	Effect of wind on atmospheric deposition .....	149
8.2.8.	A web-based model predicting atmospheric pollutant loads in stormwater .....	150
<b>REFERENCES .....</b>		<b>151</b>
Appendix A - Process-Based Models .....		174
Appendix B - Split Regression Models for Small and Large Rain Events .....		176
Appendix C - The Effect of PM on Wet Deposition and Bulk Deposition Concentrations .....		178

## TABLE OF FIGURES

Figure 1-1 Pollutant transport to urban waterways via atmospheric deposition. ....	3
Figure 2-1 Differences in peak flow and lag time following a rain event in an urban versus a rural catchment (modified from Lindh (1972)). ....	8
Figure 3-1 Top view of an impermeable board. ....	27
Figure 3-2 A RTV strip and a plastic piece used to channel runoff into the stormwater collection system. ....	27
Figure 3-3 Side and top view of the stormwater collection funnel for the concrete boards.....	29
Figure 3-4 Development of the bottom (left) and the top (right) section of the stormwater collection system for the impermeable asphalt boards. ....	30
Figure 3-5 The permeable paver stormwater collection system. Where (1) is a nylon support tray for the PCon (2) is a PVC funnel; and (3) is a supporting structure for the PVC funnel and the PCon. ....	33
Figure 3-6 Laser scanned vertically exaggerated topographical images of each pavement type. ....	34
Figure 3-7 Air (S43 30.063 E172 31.222), Res (S43 31.390 E172 35.290), and Ind (S43 34.145 E172 41.252) monitoring sites in Christchurch, New Zealand. ....	37
Figure 3-8 Smog over Christchurch City. ....	37
Figure 3-9 The distance between the concrete boards and the neighbouring buildings on (a) Ind and (b) Res (a) Buildings A and B are three stories high; (b) Houses A and B are two stories high.....	38
Figure 3-10 Wet deposition sampler deployed at the Woolston air monitoring station - the center of the industrial catchment.....	44
Figure 4-1 Benefits of (b) permeable pavements over (a) conventional impermeable pavements (modified from Sansalone et al. (2008)). ....	58
Figure 4-2 Permeable pavement systems design with an underdrain: (a) porous pavement (i.e. Open-Graded Porous Asphalt or Porous Concrete), (b) modular interlocking concrete bricks with external drainage cells. Adapted from (Auckland Council). ....	59
Figure 4-3 A PCon and OGPA pavement. ....	60
Figure 4-4 The pavement setup in the residential land-use area. ....	64

Figure 4-5 A comparison of total Cu, Zn, Pb and TSS loadings in wash-off from different pavement surfaces and from bulk deposition. The box represents the 25 <sup>th</sup> (lower) percentile, median, and 75 <sup>th</sup> (upper) percentile; the whiskers represent the 5 <sup>th</sup> and 95 <sup>th</sup> percentiles. Note the varying scales for each pollutant. ....	68
Figure 4-6 A comparison of pH and alkalinity in wash-off from different pavement surfaces and from bulk deposition. The box represents the 25 <sup>th</sup> percentile, median, and 75 <sup>th</sup> percentile; the whiskers represent the 5 <sup>th</sup> and 95 <sup>th</sup> percentiles. Where N/A = not analysed. ....	69
Figure 4-7 Image illustrating the reduced surface tension (foam on top of the samples) of runoff from Asp and OGPA, and the difference in runoff colour between the pavement types. ....	72
Figure 4-8 Changes to (a) pH and (b) alkalinity from PCon throughout the sampling campaign.....	77
Figure 4-9 Changes to Zn loads per antecedent dry day from the asphalt pavement (Asp) throughout the sampling campaign. The low Zn load on sampling event two (circled) was associated with the low rainfall that occurred for that sampling event (0.8 mm). ....	80
Figure 4-10 Changes to pH from the permeable asphalt pavements (OGPA) throughout the sampling campaign. ....	81
Figure 5-1 Airborne pollutant loads in stormwater runoff from 24 different dates when rainfall occurred in all three receptor sites - the rainfall characteristics of each date will slightly differ between land-use areas due to localised rainfall patterns within each the catchment.....	91
Figure 5-2 Wind rose plots for each experimental site along a 120° transit line, where the x-axis represents the frequency (%) of occurrence.....	93
Figure 5-3 The Ind testing site was located next to a hill.....	94
Figure 5-4 Wind speed and wind direction for the (a) Ind (b) Air and (c) Res land-use areas from the period of January 2013 to December 2013. The wind rose plot indicates the frequencies of winds blowing from an angle to the experimental site and coded bands indicating the wind speed range .....	95
Figure 5-5 Total Cu, Zn, and Pb loads per antecedent dry day from February to December 2013. The results indicate no temporal variability throughout the 11 month period. ....	98
Figure 6-1 Measured and modelled results (combined calibration and validation data) of atmospheric pollutant loads in stormwater runoff from (a) Air, (b) Ind, and (c) Res. ....	122



Figure 6-2 Estimated changes in pollutant loads based on the models generated versus measured pollutant loads. ....	125
Figure 7-1 Emissions sources of PM <sub>10</sub> and PM <sub>2.5</sub> , including a breakdown of emissions from home heating appliances contributing to PM <sub>10</sub> and PM <sub>2.5</sub> concentrations. Data based on a typical winter (Jun-Aug) weekday in Christchurch City in 2009 (Smithson 2011). ....	130
Figure 7-2 Fine and coarse particulate matter concentrations over the sampling period and rainfall depth. ....	134
Figure 7-3 (a) the quantity of total Cu in BD and WD; (b) the contribution of total and dissolved Cu in BD; and (c) the contribution of total and dissolved Cu in WD. ....	139
Figure 7-4 (a) the quantity of total Zn in BD and WD; (b) the contribution of total and dissolved Zn in BD; and (c) the contribution of total and dissolved Zn in WD. Zn loads in WD from rain event 2 (circled) is not represented it was below detection limit. ....	140
Figure 7-5 The quantity of total Pb in BD and WD. Dissolved Pb was not represented as it was frequently below detection limits. ....	140

## TABLE OF TABLES

Table 2-1 Average stormwater concentrations (data from O’Sullivan et al. (2012)) compared with the 90% ANZECC ecotoxicological guidelines. ....	11
Table 2-2 Primary sources of heavy metal pollutant in an urban environment (Auckland Regional Council 2005). ....	12
Table 2-3 Metal leaching concentrations from Cu roofs. Where ‘N/A’ = not available. ....	12
Table 2-4 Zn leaching concentrations from various Zn-based roofs. ....	13
Table 2-5 Sources of heavy metals from vehicles in urban runoff. Modified from Sansalone and Buchberger (1997). Where x = primary source and ** = secondary source. ....	14
Table 2-6 Average concentrations or loadings of Cu, Zn, and Pb in atmospheric deposition (wet, bulk, & dry deposition) as reported in literature. Where “n/a” = not available. ....	17
Table 3-1 Types of samplers used to monitor the contribution of the atmospheric deposition in stormwater. ....	22
Table 3-2 Impermeable concrete recipe for one board - equivalent to 0.018 m <sup>3</sup> of concrete. .	25
Table 3-3 Permeable concrete recipe for one board - equivalent to 0.014 m <sup>3</sup> of concrete. ....	32
Table 3-4 Surface roughness characteristics from the different pavement types. ....	33
Table 3-5 Information regarding the collection of weather data. ....	41
Table 3-6 Monthly rainfall amounts (mm) during each research component compared to the average monthly rainfall from the previous 10 years (mean ± S.E.). Where “-” represents months where no research was conducted; blue colour represents months of atypical low rainfall; and red colour represents months of atypical high rainfall. ....	42
Table 3-7 Component 1 (spatial and temporal variations) prediction models for TSS. ....	45
Table 3-8 Parameters that were analysed after a rain event of certain depth and the minimum runoff volume required for analyses. ....	46
Table 3-9 Preservation methods and maximum holding times (APHA 2005). ....	49
Table 4-1 Background pollutant concentrations from the different pavement types (minus the pollutant concentrations from the feed water used by the rainfall simulator). pH of the feed water was 6.7. TSS was below the detection limits. ....	65
Table 4-2 Rainfall characteristics of each sampling event captured. Where, ADD = antecedent dry days; RD = rain depth; RI = peak hourly rain intensity over the rain event; Dur = rain	

duration. Where: * represents TSS not measured and ** represents TSS and alkalinity not measured. ....	66
Table 4-3 Pollutant load ranges from the different pavement types compared to the pollutant loads from bulk deposition (BD) and wet deposition (WD) during a sampling campaign from June 2014 to August 2014. ....	67
Table 4-4 Percentage removal (%) of metal loads from bulk deposition. ....	67
Table 4-5 The percentage contribution of dissolved to total Cu and Zn. Note, Pb was not analysed as dissolved Pb was consistently below detection limits. ....	71
Table 4-6 Average concentrations ( $\mu\text{g/l}$ ) of Cu and Zn in wash-off from each pavement type compared with the 90% ANZECC ecotoxicological guidelines and the hardness-dependent 90% ANZECC ecotoxicological guidelines for PCon only. ....	79
Table 5-1 Background pollutant concentrations (mean $\pm$ SE) from the impermeable concrete boards from each land-use area studied (minus the pollutant concentrations from the feed water used by the rainfall simulator). pH of the feed water was 6.19. ....	89
Table 5-2 Number of rain events captured that conformed to different meteorological criteria. ....	89
Table 5-3 Pollutant load ranges from the impermeable concrete boards for each land-use area studied. Note dissolved Pb was not analysed as it was frequently below the detection limit. .	90
Table 5-4 The ratio of build-up per antecedent dry day ( $\mu\text{g/m}^2/\text{d}$ ) for different elements as a ratio to Cu (mean $\pm$ SE) from each land-use area. Within each elemental group, those sharing a common letter are not significantly different ( $p > 0.05$ ); determined from a permutation MANOVA and subsequent multiple ANOVA's. ....	93
Table 6-1 The influencing variables of pollutant build-up and wash-off dynamics. ....	106
Table 6-2 Process-based models versus regression models. ....	109
Table 6-3 Relationships between meteorological characteristics and runoff quality in process-based and regression models. Where: “x” represents non-significant relationships; “Y” represents significant relationships; and “-” represents relationships not discussed in the studies. ....	110
Table 6-4 Meteorological variables used for regression analysis. ....	115
Table 6-5 Transformations applied to the independent variables. ....	115

Table 6-6 Range of weather conditions represented during the sampling campaign, where n is the number of rain events sampled. ....	117
Table 6-7 Summary of total Cu, Zn, Pb and TSS loads in runoff (mean $\pm$ S.E.). ....	117
Table 6-8 Model summary of the best fitted values for total Cu, Zn, Pb, and TSS, including the error (%) between the measured and modelled ‘validation’ data (% error). ....	121
Table 6-9 Percentage contribution (mean $\pm$ S.E.) of dissolved Cu and Zn to their total loadings. Dissolved Pb was not included as it was frequently below the detection limit. ....	125
Table 7-1 Variables influencing PM concentrations. ....	129
Table 7-2 Summary of rain events captured during the sampling campaign. ....	134
Table 7-3 The range (min – max) and mean values of particulate matter a day prior to the rain event (before rain), averaged PM concentrations over the antecedent dry period (average), and total metals in wet deposition. ....	135
Table 7-4 The range (min – max) and mean values of total metals ( $\mu\text{g}/\text{m}^2$ ) in bulk deposition from August 2013 to December 2013 and the ratio of pollutant in wet deposition to bulk deposition (%). Where “n/d” = not detected and “-” represents results not analysed due to insufficient data. ....	135
Table 7-5 The average concentrations of coarse and fine PM ( $\mu\text{g}/\text{m}^3$ ) with varying antecedent dry periods. Within each antecedent dry period, those sharing a common letter are not significantly different ( $p > 0.05$ ). Where “n” = number of cases analysed. ....	136
Table 7-6 Pearson’s correlation between PM and metals (loads) in wet deposition. ....	137

## GLOSSARY OF TERMS

ADD	Antecedent dry days
Air	Airside (of an airport) experimental site
ANOVA	Analysis of variance
ANZECC	Australian and New Zealand guidelines for fresh and marine water quality
Asp	Asphalt boards
BD	Bulk deposition
BD <sub>con</sub>	Bulk deposition loads in runoff from an impermeable concrete board
Boards	Modular paving slabs
CBD	Central business district
CIAL	Christchurch International Airport Limited
Con	Concrete boards
Cond	Conductivity
CPRS	Canterbury Regional Policy Statement
Cr	Chromium
CSOs	Combined Sewer Overflows
Cu	Copper
CWMS	Canterbury Water Management Strategy
DD	Dry deposition
DOC	Dissolved organic carbon
Dur	Rainfall duration
ECan	Environment Canterbury
Hard	Hardness
HDPE	High-density polyethylene
ICP-MS	Inductively coupled plasma mass spectrometry
Ind	Industrial experimental site
KN	Kjeldahl-N
MANOVA	Multivariate analysis of variance
MICBEC	Modular interlocking concrete bricks with external drainage cells
MICBIC	Modular interlocking concrete bricks with internal drainage cells
Mn	Manganese
NES	National Environmental Standards for Air Quality
Ni	Nickel
NPDES	National Pollutant Discharge Elimination System
NRRP	Canterbury Natural Resources Regional Plan

OGPA	Open-graded porous asphalt boards
Pb	Lead
PCA	Principal component analysis
PCon	Porous concrete pavers
PLPC	Pollution load producing coefficients
PM	Particulate matter
PM <sub>2.5</sub>	Particles smaller than 2.5 µm
PM <sub>10</sub>	Particles smaller than 10 µm
PM <sub>10-2.5</sub>	Particles between the 2.5 - 10 µm size range
PPS	Permeable pavement system
PVC	Polyvinyl chloride
RD	Rainfall depth
Res	Residential experimental site
RI	Rainfall intensity
RMA	Resource Management Act
RoNS	Roads of National Significance
RPD	Relative percentage difference
RTV	Room temperature vulcanising
Ru. rate	Runoff rate
Ru. vol.	Runoff volume
Sb	Antimony
SS	Suspended solids
SWMM	Storm Water Management Model – U.S. E.P.A.
TSS	Total suspended solids
Vol	Rainfall volume
VSS	Volatile suspended solids
WD	Wet deposition
WD <sub>1</sub>	Wind direction prior to rainfall
WD <sub>2</sub>	Wind direction during rainfall
WDS	Wet deposition sampler
WFD	Water Framework Directive
WHO	World Health Organisation
WS <sub>1</sub>	Wind speed prior to rainfall
WS <sub>2</sub>	Wind speed during rainfall
Zn	Zinc

## RESEARCH OUTPUTS

### *Journal Papers*

- (1) Murphy, L. U., O'Sullivan, A., & Cochrane, T. A. (2014). Quantifying the spatial variability of airborne pollutants to stormwater runoff in different land-use catchments. *Water, Air, & Soil Pollution*, 225(7), 1-13.
- (2) Murphy, L. U., Cochrane, T. A., & O'Sullivan, A. (2015). Build-up and wash-off dynamics of atmospherically derived Cu, Pb, Zn and TSS in stormwater runoff as a function of meteorological characteristics. *Science of the Total Environment*, 508, 206-213.
- (3) Murphy, L. U., Cochrane, T. A., & O'Sullivan, A. (in press). The influence of different pavement surfaces on atmospheric copper, lead, zinc, and suspended solids attenuation and wash-off. *Water, Air, & Soil Pollution*.

### *Conference Papers*

- (1) Murphy, L. U., O' Sullivan, A., Cochrane, T. A. (2014). The influence of meteorological characteristics on atmospheric contaminant loadings in stormwater runoff at an international airport. In: World Environmental & Water Resources Congress 2014 Proceedings, Portland, U.S, June 1-5, 2014, pp. 75-84.
- (2) Murphy, L. U., O' Sullivan, A., Cochrane, T. A. (2014). The spatial and temporal variability of airborne pollutants in stormwater runoff. In: Proceedings of the 9<sup>th</sup> South Pacific Stormwater Conference, New Zealand Water Association, Christchurch, New Zealand, May 14-16, 2014.

### *Conference Abstracts (Oral Presentations)*

- (1) Murphy, L. U., O' Sullivan, A., Cochrane, T. A. (2013). Quantifying Spatial and Temporal Deposition of Atmospheric Contaminants in Runoff from Concrete Pavements. Waterways Postgraduate Student Conference, Nov 12, 2013.
- (2) Murphy, L. U., Cochrane, T. A., & O'Sullivan, A. (2014). The influence of pavement type on airborne pollutant wash-off. Waterways Postgraduate Student Conference, Nov 18, 2014.

# Chapter One: Introduction



## **1. INTRODUCTION**

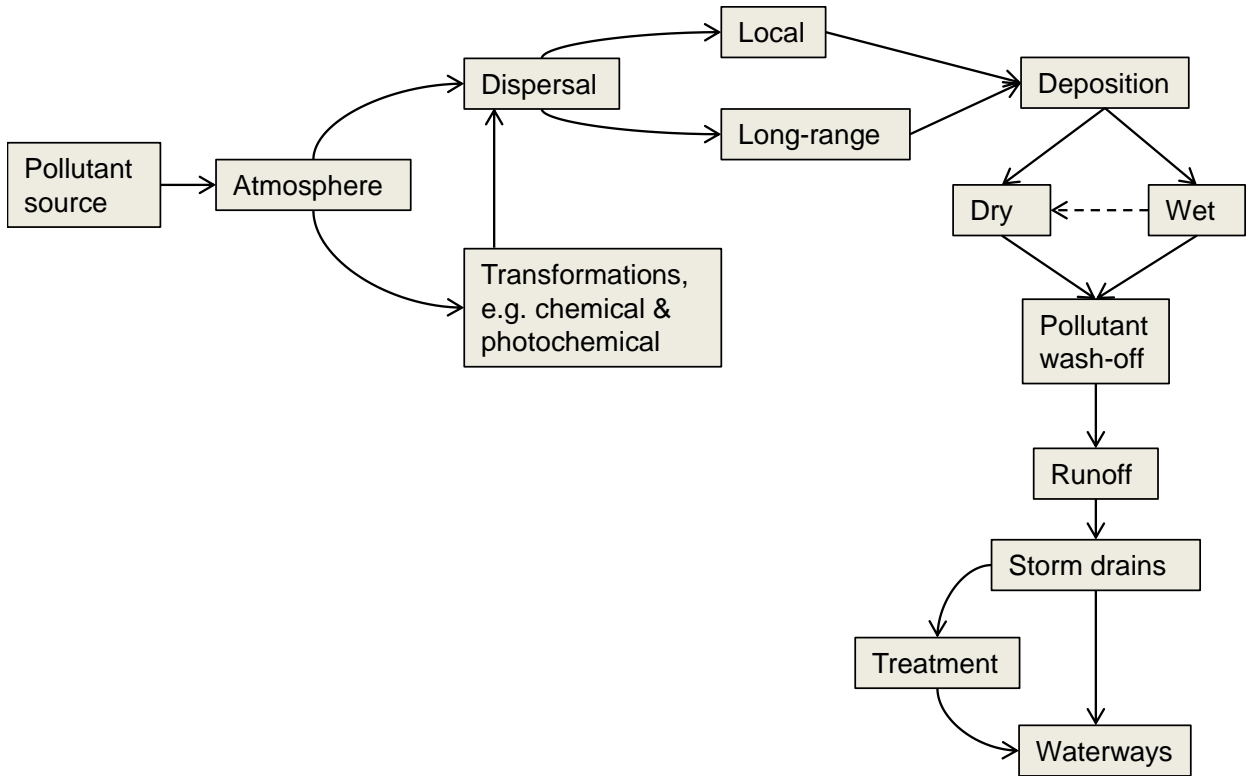
### **1.1. Statement of Problem**

Runoff from urban surfaces is one of the primary causes of water quality degradation in urban waterways (Lee and Bang 2000). Pollutants are transported in stormwater runoff to nearby waterways, thereby, negatively effecting aquatic ecosystems (Beck and Birch 2011). In most cases, stormwater managers solely focus on the *direct* pollution of urban runoff within a catchment (e.g., from vehicular activity and metal roof erosion) when implementing stormwater abatement strategies. *Indirect* pollution from atmospheric deposition is rarely considered. This is due to the uncertainty and challenges associated with measuring and managing these contributions (Aryal et al. 2010). However, airborne deposition can contribute substantial pollutant amounts in runoff (Sabin et al. 2005). For the semi-arid catchment of Los Angeles, U.S.A., atmospheric deposition can potentially account for between 57-100% of the metal loadings in stormwater signatures (Sabin et al. 2005). Davis and Birch (2011) found that atmospheric deposition contributed to 33%, 12%, and 5% of Zn, Cu, and Pb, respectively, in runoff (calculated based on respective event mean concentrations) from an urban catchment in Sydney, Australia. Currently, there is no information regarding how much atmospheric deposition contributes to total stormwater pollution in New Zealand.

### **1.2. Atmospheric Pollutant Transport to Waterways**

The process describing how atmospheric pollutants are transported into waterways is exemplified in Figure 1-1. Pollutants are emitted into the atmosphere from either natural or anthropogenic sources. These pollutants can undergo various transformations (e.g. chemical and photochemical) to form secondary pollutants. Both the primary and secondary pollutants are dispersed around the atmosphere, where they either can be transported locally or can be transported long distances away from their emission source. Eventually, the pollutants are removed from the atmosphere via dry or wet deposition. When atmospheric pollutants deposit onto urban surfaces, they can be washed-off and incorporated into stormwater runoff

following a precipitation event. The stormwater runoff is directed into nearby waterways with or without prior treatment.



**Figure 1-1 Pollutant transport to urban waterways via atmospheric deposition.**

### 1.3. Purpose of Research

There remains a dearth of knowledge regarding the significance of airborne pollutants (i.e. Cu, Zn, Pb, and TSS) in stormwater. Limited studies have monitored the effects of land-use activity on atmospherically-derived metal pollutants in runoff. However, no study has monitored this from an airport's airshed. In addition, the influence of a hillslope on atmospheric pollutant loads in stormwater has not been previously studied. Limited studies have monitored and modelled atmospheric pollutant wash-off from an impermeable pavement surface with varying meteorological conditions (Wicke et al. 2010; Wicke et al. 2012a; Wicke

et al. 2012b); however, no other study has monitored this under natural rainfall conditions. Monitoring atmospheric pollutant wash-off under natural rainfall conditions is essential to account for wet deposition loads and rainfall variability (i.e., altering rainfall intensities and depths). Moreover, relatively little information is available on how atmospheric pollutants are washed-off from different pavement materials (impermeable concrete and impermeable asphalt). The performance of permeable concrete and asphalt pavements at attenuating atmospheric pollutants have not been previously studied. Therefore, research was undertaken in this Thesis to increase our knowledge on the factors governing atmospheric pollutant loads in stormwater.

### ***1.3.1. Scope of objectives***

The aim of this research was to quantify the spatial and temporal variability of atmospherically derived pollutants in runoff from different pavement types.

In this research, the following questions were addressed:

- i. What effect does different impermeable pavement types have on pollutant retention and wash-off?
- ii. How effective are different permeable pavements at retaining airborne pollutants during infiltration?
- iii. What is the spatial variability of urban atmospheric pollutant deposition in runoff between different land-use areas?
- iv. What effect do different meteorological variables have on airborne pollutant build-up and wash-off; can this information be used to predict atmospherically derived pollutant loads in stormwater?
- v. How much does wet deposition contribute to the atmospheric pollutant deposition loads? What is the relationship between wet deposition and atmospheric particulate matter concentrations?

To address these objectives, modular paving slab systems were exposed to atmospheric pollutant build-up. After a rain event, the atmospheric pollutants were washed-off. The wash-off was collected and analysed for the key stormwater pollutants: Cu, Zn, Pb and total suspended solids. Modular concrete paving slab systems were deployed in three land-use areas (residential, industrial, and airside) simultaneously over a long period. This enabled the contribution and trends of atmospheric pollutants in stormwater to be analysed over varying spatial and temporal conditions; therefore, their influence on atmospheric pollutant deposition dynamics could be quantified. In addition, atmospheric pollutant build-up and wash-off dynamics from different pavement materials (permeable asphalt, impermeable asphalt, permeable concrete, and impermeable concrete) were analysed and the atmospheric pollutant retention capabilities of each pavement type were quantified.

#### **1.4. Scope of Thesis**

The body of this Thesis has the following structure: Chapter 2 will provide a background on stormwater pollution and atmospheric deposition that drives the purpose of this research. Chapter 3 presents details on the methodology employed. Chapter 4 provides a study on the effects of pavement type on pollutant runoff. It will also discuss the efficiency of permeable concrete and asphalt at removing pollution loads. Chapter 5 describes the spatial variation of atmospheric pollutants in stormwater runoff. It compares the results of pollutant loads from three land-use areas (industrial, residential, and airside) and discusses the potential sources of atmospheric metal pollution in the Christchurch airshed. Chapter 6 provides an analysis of the meteorological variables controlling pollutant build-up and wash-off. It also presents a novel statistical technique for generating pollution prediction models. Chapter 7 discusses the relationships between wet deposition and particulate matter. In addition, the contribution of wet deposition to the total deposition flux for the industrial land-use area is discussed. Chapter 8 provides a conclusion to the key outcomes of this research and provides recommendations for future work. Specific literature reviews are provided in each results chapter.

# Chapter Two: Background

## **2. BACKGROUND**

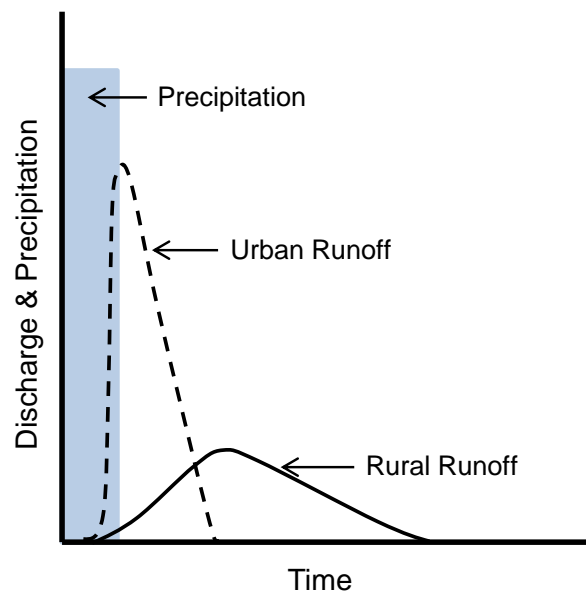
### **2.1. Urban Stormwater Runoff**

In an undisturbed hydrological cycle, precipitation is temporarily detained by soils, which eventually infiltrates to groundwater aquifers. Some precipitate may also be redirected back to the atmosphere via evapotranspiration, with only a small portion flowing over the land surface as sheet runoff (Lindh 1972). Urbanisation interrupts the flow of this hydrological cycle by creating an impermeable barrier to natural infiltration. Rainwater, now unable to infiltrate, is redirected (frequently untreated) to nearby waterways as runoff (Göbel et al. 2007; Brown et al. 2013). This alters the water quality and quantity of the receiving waterway, thereby adversely affecting aquatic ecosystems. These changes are known as the “Urban Stream Syndrome” (Meyer et al. 2005; Walsh et al. 2005). The urban stream syndrome is characterised by: flashier hydrology, i.e., the accelerated onset and decline of stream flows, faster and higher peak stormwater discharges (Farahmand et al. 2007); modified stream morphology and stability; amplified concentrations of pollutants and; reductions in aquatic biodiversity with an increased abundance of tolerant species (Walsh et al. 2005). The effects are so damaging that stormwater, the principle cause of the urban stream syndrome (Roy and Bickerton 2011), is regarded as a more serious pollution threat than municipal waste in certain areas (Sartor et al. 1974). Even in a catchment with only 10% impervious cover, some degradation of the waterway will occur; at 30%, water degradation is certain (Arnold and Gibbons 1996). With half the world’s population predicted to reside in urban areas by 2020, imperviousness, and hence runoff, will undoubtedly increase (Aryal et al. 2010).

#### **2.1.1. *Physical responses***

Impermeabilisation, and consequently the increase in surface runoff through constructed drainage systems, is the principal cause of hydrological changes to waterways (Walsh et al. 2005). Before urbanisation, stormwater was detained by the soils reservoir capability and slowly released; after urbanisation, stormwater rapidly flows into the nearest waterway in

intense bursts of discharge (Booth and Leavitt 1999). Reductions in unit-hydrograph width, as shown in Figure 2-1, demonstrates the efficiency of drainage systems to quickly direct large volumes of runoff away from urbanised areas (Seaburn 1969). Hence, the time between peak precipitation volume to peak runoff is shorter, resulting in rapid flooding (Paul and Meyer 2001; Espey et al. 1966). This flooding has traditionally been recognised as an important stormwater issue because it directly effects human activity (Park et al. 2014). In addition to rapid flooding, flood peak widths are reduced resulting in shorter flood durations (Paul and Meyer 2001). Urbanisation also impact's groundwater hydrology, because aquifer recharge, via infiltration, is inhibited (Erickson and Stefan 2009). This can diminish stream base flows that can be essential for maintaining flow during dry periods (Dunne and Leopold 1978).



**Figure 2-1 Differences in peak flow and lag time following a rain event in an urban versus a rural catchment (modified from Lindh (1972)).**

Urbanisation is also responsible for the altered geomorphology of streams and river channels. Urbanisation has a three-stage cycle that results in river channel modifications, as stated by Wolman (1967). They are: 1) the pre-development stage consisting of a stable waterway; 2) the construction stage resulting in increased erosion of exposed soils; and 3) the post-

development stage expressed by impermeable pavements, roofs, stormwater drains, and sewerage systems. The repercussion of the construction stage is a short-term increase in sediment loadings into river channels (Wolman 1967; Chin 2006), and consequently, results in rapid aggradation of waterways and elevated sediment fill (Paul and Meyer 2001; Wolman 1967). Following the construction stage, sediment yields typically decrease to values lower than pre-development conditions (Wolman 1967). Additionally, the increase in impervious surfaces results in greater runoff generation. The combined runoff and decreased sedimentation results in channel erosion and channel enlargement (Chin 2006). A study conducted by Neller (1988) exemplifies channel erosion/enlargement, it found that knickpoint (abrupt steepening of slope) retreat was 2-4 times greater in an urban catchment versus its rural counterpart. Similarly, bank erosion was 3-6 times greater in an urban catchment.

### **2.1.2.      *Biological responses***

Unsurprisingly, aquatic ecosystems are adversely impacted from the physical (and chemical) changes imposed by urbanisation (Gurnell et al. 2007). These changes restructure aquatic communities and result in a decrease in the productivity and diversity of fish and invertebrates (Wang et al. 2003). With only a 10% effective impermeable area, there is a demonstrable loss of aquatic ecosystem function that is potentially irreversible (Booth and Jackson 1997). Whiting and Clifford (1983) found that upstream of an urban catchment in Alberta, Canada, an abundance of invertebrates existed, e.g. *Gammarus lacustris* and *Simulium* spp., which were rare or absent in the urban stream. Additionally, the richness of macroinvertebrate fauna in the urban stream was poor, with tubificids accounting for 72% of the macroinvertebrates found. Duda et al. (1982) found that the average number of different fauna per square metre was reduced by 75-80% in urban areas compared to upstream levels. Furthermore, stormwater runoff, particularly from residential areas, can be a source of bacteria and faecal coliforms to streams that can have adverse effects on human health (Bannerman et al. 1993).



### **2.1.3.      *Chemical responses***

Although impervious surfaces are not always a source of pollutants themselves, they are efficient conveyors of polluted stormwater runoff (Arnold and Gibbons 1996). As stormwater flows over the impervious land surface, pollutants from the land are carried with it; thus, compromising the quality of the stormwater. Stormwater signatures typically comprise of suspended sediments (SS) from building and pavement weathering; heavy metals from weathered building materials, wear and tear from vehicle components; hydrocarbons from industrial and vehicle emissions; and nutrients from excessive fertiliser usage on vegetation (Davis et al. 2010a). In New Zealand, sediments and heavy metals are of greatest concern due to their dominance in stormwater signatures and their detrimental effects on aquatic ecosystems (Auckland Regional Council 2003; CCC 2003). The concentration of these pollutants in stormwater can vary significantly with factors such as the season, number of antecedent dry days, and the duration and volume of rainfall (Waara and Färm 2008). It is believed that a disproportionately large fraction of pollutants are typically removed during the initial stage of runoff from a new rain event, known as the first flush effect (Characklis and Wiesner 1997). This first flush can result in a significant shock to an aquatic ecosystem and it is likely that it occurs for every rain event (Barry 2006).

#### **2.1.3.1. *Total suspended solids***

Total suspended solids (TSS) in urban runoff is regarded as an important pollutant with adverse impacts on receiving waterways (Shammaa et al. 2002). Increased sediment deposition can adversely affect invertebrate communities. Sediments reduce interstitial space resulting in reduced habitat; clog gills; decrease attachment points for invertebrates; reduce oxygen and metabolite exchange for biota living in the benthos; alter the quantity and quality of benthic food supplies; and decrease biodiversity (Suren 2000; Ryan 1991). Turbidity (a decrease in water clarity due to the presence of TSS (Ziegler 2002)) reduces photosynthesis limiting overall community productivity. Additionally, sediments are a sink for pollutants (e.g. heavy metals), but can also function as a source of pollutants to an ecosystem (Beasley

and Kneale 2002) depending on the physio-chemical condition (i.e. at low pH) of the waterway. Macro-invertebrates, which serve as the food supply for fish and other large aquatic organisms, are particularly vulnerable to sediment pollution (Beasley and Kneale 2002).

#### 2.1.3.2. Heavy metals

Heavy metals are elements with densities exceeding  $5.0 \text{ g cm}^{-3}$ ; they are typically affiliated with pollution and toxicity and can be absorbed by organisms at low concentrations (Adriano 2001). Heavy metals are one of the leading causes of water degradation because of their toxic and persistent nature (Thamer et al. 2012). They do not biodegrade, can accumulate in the environment (Vollertsen et al. 2009) and in living tissue (bioaccumulation), ultimately, threatening predators at trophic levels higher up the food chain (Beasley and Kneale 2002). Metals in their dissolved form are most concerning because of their increased mobility in the aquatic environment, and thus, availability for biological uptake (Vollertsen et al. 2009). The heavy metals Cu, Pb, and Zn are of particular concern due to their dominance in urban runoff signatures in New Zealand (Zanders 2005) and elsewhere. For example, in Christchurch, New Zealand, stormwater entering the Okeover Stream typically exceeds the Australian and New Zealand guidelines for fresh and marine water quality (ANZECC) (2000) 90% species protection levels<sup>1</sup> many-fold (e.g. Table 2-1) (O’Sullivan et al. 2012). The sources of heavy metals to the urban environment are exemplified in Table 2-2.

**Table 2-1 Average stormwater concentrations (data from O’Sullivan et al. (2012)) compared with the 90% ANZECC ecotoxicological guidelines.**

Metal	90% ANZECC ( $\mu\text{g/l}$ )	Stormwater ( $\mu\text{g/l}$ )	
		Total	Dissolved
Zn	15.0	$271.0 \pm 39.0$	$153.0 \pm 54.0$
Cu	1.8	$16.0 \pm 12.0$	$4.0 \pm 2.0$
Pb	5.6	$26.0 \pm 7.0$	$0.90 \pm 0.30$

<sup>1</sup> ANZECC 90% protection level: derived trigger values for toxicants, which if not exceeded 90% of the aquatic species in a freshwater ecosystem will be protected (ANZECC, 2000)

**Table 2-2 Primary sources of heavy metal pollutant in an urban environment (Auckland Regional Council 2005).**

Pollutant	Primary sources
Zn	Galvanised roofs and other construction materials, paints, industry, tyres
Cu	Vehicle brakes, water pipes, industry, copper roofs
Pb	Industry, remnants from lead-based paints and petrol

#### **2.1.4. Direct sources of Cu, Pb, and Zn to stormwater runoff**

Building (roof and sidings) and road runoff are considered the major *direct* sources of heavy metals (especially Cu and Zn) in urban runoff. Roofing materials such as rolled Cu and Zn are widely used as they are considered relatively “maintenance-free”, durable, and can be adapted to many different design styles (He et al. 2001). Lead can also be found in roofing materials, for example, a slate roof with lead fittings contributed 1.1 mg/m<sup>2</sup>/day of Pb in roof runoff (Rocher et al. 2004). These roofing materials are subject to natural atmospheric corrosion processes and can be a significant source of heavy metal pollution (see Table 2-3 & Table 2-4). Building sidings can contribute substantial quantities of heavy metals to stormwater, for example, contributing 22%, 59%, and 79% of Cu, Zn, and Pb in urban residential runoff (Davis et al. 2001).

**Table 2-3 Metal leaching concentrations from Cu roofs. Where ‘N/A’ = not available.**

Author	Location	Age	Cu	Units
<i>Pennington &amp; Webster-Brown (2008)</i>	Auckland, New Zealand	New	1,140 – 6,830	µg/l
		30 yr	742 – 4,000	
<i>Karlén et al. (2002)</i>	Stockholm, Sweden	New	1,800 – 3,900	µg/l
		30 yr	2,400 – 5,400	
<i>Boulanger &amp; Nikolaidis (2003)</i>	Connecticut, USA	6-10 yr	3,630 ± 1,760	µg/l
		N/A	1,340 ± 820	
		67-69 yr	1,460 ± 840	
<i>Wicke et al. (2014)</i>	Christchurch, New Zealand	53 yr	5,794 - 10,600	µg/l
		45 yr	6,367 – 13,800	

**Table 2-4 Zn leaching concentrations from various Zn-based roofs.**

Author	Location	Age/Type	Zn	Units
<i>Lindstrom &amp; Wallinder (2011)</i>	Stockholm, Sweden	Galv. steel	≈ 4,478 <sup>a</sup>	µg/l
<i>Clark et al. (2008)</i>	Eastern U.S.A.	Galv. metal	5,000 – 30,000	µg/l
		Painted Al-Zn	< 250	
<i>Karlén et al. (2001)</i>	Stockholm, Sweden	Various <sup>b</sup>	40 – 6,800	µg/l
<i>Wicke et al. (2014)</i>	Christchurch, New Zealand	Galv. Fe (55yr)	1,325 – 7,900	µg/l
		Galv. Fe (15yr)	1,266 – 4,400	

<sup>a</sup> estimated from data supplied, <sup>b</sup> various number of commercially available Zn-based construction materials

Roads are estimated to contribute between 35-75% of heavy metals in urban runoff, although they only comprise approximately 10-20% of an urban catchment (Pandey et al. 2005). Birmili et al. (2006) found that roadside particular matter has Ba, Cu, Fe, Na<sup>+</sup>, Ca<sup>2+</sup>, Al, Mg<sup>2+</sup> concentrations 14 times higher than urban background levels. Metal pollutants on road surfaces (Table 2-5) originate from tyre wear, brake lining, exhaust fumes, road construction, resuspension of road dust, car catalysts, and road paint (Adachi and Tainosho 2004; Sternbeck et al. 2002; Beasley and Kneale 2002). Tyre wear is recognised as a significant contributor of Zn to the environment; representing 25% of the Zn loads found in urban residential stormwater (Davis et al. 2001). Zinc oxide (ZnO) is added as a vulcanising agent to the rubber compound in tyres (Smolders and Degryse 2002). The weighted average for ZnO in the tread (the part exposed to wear) of a car tyre and truck tyre are 1.2% and 2.1% respectively. Copper is contained in brake pads due to its excellent thermal conductivity; thus, controlling the maximum surface temperature and reducing the likelihood of system overheating (Österle et al. 2010). However, when forced to decelerate, large frictional heat is generated in the brakes, which generates brake pad particles (and thus Cu particles) that are subsequently released into the environment (Hulskotte et al. 2007). Davis et al. (2001) found that brake emissions were the largest contributor of Cu in urban runoff, representing 47% of the total Cu loads. Consequently, to protect their aquatic ecosystems, California has introduced Senate Bill 346 (2013) banning the sale of brake friction materials surpassing 0.5% Cu by weight by 2025.

**Table 2-5 Sources of heavy metals from vehicles in urban runoff. Modified from Sansalone and Buchberger (1997). Where x = primary source and \*\* = secondary source.**

	Brakes	Tyres	Frame & body	Fuels & oils	De-icing salts	Litter
<i>Cd</i>	**	x				
<i>Cr</i>		x				
<i>Cu</i>	x	x				
<i>Fe</i>		x	x			x
<i>Pb</i>	**	**		**	**	
<i>Ni</i>		x				
<i>V</i>				x		
<i>Zn</i>	x	x	x			

The majority of pollutants from road traffic (80-95%) are not directly deposited onto the road surface; instead, they are carried away by wind and spray action to elsewhere in the local vicinity (Göbel et al. 2007). Therefore, atmospheric deposition can be a significant *indirect* source of heavy metals in urban runoff (Hu and Balasubramanian 2003).

## 2.2. Atmospheric Deposition

The transfer of elements through the atmosphere is a fundamental process in the biogeochemical cycle of the environment (Galloway et al. 1982; Azimi et al. 2003). Elements are emitted into the atmosphere from different natural or anthropogenic activities and can be returned to the earth's surface as atmospheric deposition (Hendry and Brezonik 1980). Atmospheric deposition occurs in two ways: dry or wet deposition. Dry deposition is the direct settling of particles and gases onto land or water surfaces via gravitational settling, impaction, turbulence, or Brownian motion depending on the size of the particle (Shrivastav 2001; Azimi et al. 2003). Dry deposition occurs in three steps: 1) aerodynamic transport, i.e. the transport of particles from the lower atmosphere to the boundary layer; 2) transport around the boundary layer and; 3) chemical and/or physical interaction of particles with the surface (Fang 1998). Wet deposition occurs when pollutants leach from the atmosphere with water droplets in the form of rain, fog, mist, dew, snow, and frost (Göbel et al. 2007) and it is

considered the cleanser of the atmosphere (Hendry and Brezonik 1980). Wet deposition occurs in two processes: in-cloud and below-cloud scavenging. Below-cloud scavenging occurs when particulates are collected by falling raindrops, i.e. impact scavenging (Shrivastav 2001). In-cloud scavenging is a combination of impaction and nucleation scavenging (Zhang and Vet 2006). Wet deposition can include both particulate and dissolved matter which phase elements partition into is primarily based on the emitted form, the rain pH, and the solubility of the element (Conko et al. 2004). Dry deposition dominates the  $>8.4 \mu\text{m}$  size fraction (Chester et al. 1999), while wet deposition is most efficient at scavenging the 2-10  $\mu\text{m}$  size fraction (Zhang and Vet 2006). Dry deposition is more effected by its source characteristics than wet deposition as particles scavenged by wet deposition are smaller and have a greater capability to travel farther from their source (Gunawardena et al. 2013). In arid and semi-arid regions, dry deposition is the major pollutant pathway contributing 90-99% to the total deposition flux due to the limited precipitation (Sabin et al. 2006, 2005). Although dry deposition is a slow process, it is continually occurring unlike wet deposition; therefore, it can be of greater importance for net pollutant deposition (Zhang and Vet 2006). Dry deposition will dominate the total deposition flux particularly in areas of low rainfall. Atmospheric deposition plays a vital role in the urban cycle of metals and can contribute to urban runoff pollution (Garnaud et al. 1999).

Emission of heavy metals into the atmosphere (which are ultimately deposited as atmospheric pollutants) can originate from natural or anthropogenic sources. Natural sources include volcanoes, sea salt spray, forest fires, and soil erosion (Lamprea and Ruban 2011). Anthropogenic sources include traffic fuel combustion, industry, construction sites, heating, waste incineration, and agriculture (Fang et al. 2007b; Lamprea and Ruban 2011). Anthropogenic sources tend to be highly localised and elevated, particularly in industrial and urban catchments (Fang et al. 2007b). For instance, the mean annual atmospheric heavy metal concentrations are 3-9 times greater in urban areas than in rural areas, due to higher source emissions (Sabin et al. 2006). Additionally, concentrations of heavy metals are highest in the smaller size ranges due to a larger surface area for metal adsorption (Camponelli et al. 2010); with particles  $<6 \mu\text{m}$  affiliated with the majority of metal mass (Lim et al. 2006). As atmospheric particulates originating from anthropogenic sources have a size distribution from

0.001  $\mu\text{m}$  to 50  $\mu\text{m}$  (Shrivastav 2001), airborne particulates can contribute high metals loadings to the environment. In particular, vehicular emissions, road dust resuspension, and industrial emissions are the major contributors of atmospheric metals (Shah et al. 2006; Manoli et al. 2002). Although high temperature industrial processes (e.g. coal and oil combustion, waste incineration, cement production, non-ferrous metal, iron, and steel production) are reported as important contributors of atmospheric metals in Europe and the U.S., New Zealand has a limited number of these industrial processes, and therefore, they are unlikely to contribute significantly to the atmospheric metal flux (Gray et al. 2003).

Atmospheric metals can be transported long-distances or be deposited locally to the urban ecosystem (Conko et al. 2004). For the Pb and Cd, they are transported over a regional scale because of their long-range dispersal (Bringmark et al. 2013). However, as metal particles that originate from urban sources usually have a heavier mass they are deposited near their source due to gravitational settling (Conko et al. 2004). For example, the deposition fluxes of heavy metals in Paris, France, were 2,300 - 2,800  $\text{mg ha}^{-1} \text{ day}^{-1}$  (Rocher et al. 2004). Further information regarding metals fluxes in atmospheric deposition is detailed in Table 2-6. These airborne particulates deposit onto impervious surfaces during antecedent dry days and are subsequently transported to waterways as urban runoff following precipitation events (Burian et al. 2001). Once the airborne particulates are washed off, they are known as suspended solids (Aryal et al. 2010). Atmospheric deposition is a significant source of waterway pollution, especially in areas where large amounts of metals and other pollutants are released into the atmosphere (Sabin et al. 2006; Fang et al. 2007b). Since dissolved metals can be found in atmospheric deposition, it is important to quantify their contribution to stormwater runoff for developing appropriate treatment strategies targeting dissolved or particulate metals (Hu and Balasubramanian 2003).

**Table 2-6 Average concentrations or loadings of Cu, Zn, and Pb in atmospheric deposition (wet, bulk, & dry deposition) as reported in literature. Where “n/a” = not available.**

	Author	Place	Units	Cu	Zn	Pb
<i>Wet</i>	Hendry and Brezonik (1980)	Florida, U.S. (urban)	µg/l	39.4	28.2	15.2
	Halstead et al. (2000)	Paradise, New Zealand (rural)	µg/l	13	38	20
	Conko et al. (2004)	Virginia, U.S.A. (urban)	µg/l	0.76 ± 1.2	4.4 ± 3.4	0.5 ± 0.6
	Muezzinoglu & Cizmecioglu (2006)	Izmir, Turkey (suburban)	µg/l	19.7 ± 25	186.4 ± 225	7.0 ± 4.1
	Deboudt et al. (2004)	Northern France (semi-rural)	µg/l	89 ± 120.7	1425 ± 2583	580.2 ± 601
	Hu and Balasubramanian (2003)	Singapore	µg/m <sup>2</sup> /yr	14,560	18,720	8,840
	Sabin et al. (2005)	Los Angeles, U.S. (urban)	mg/m <sup>2</sup> /yr	0.2	1.5	0.03
<i>Bulk</i>	Hendry and Brezonik (1980)	Florida, U.S. (urban)	µg/l	32.6	193.8	11.6
	Hou et al. (2005)	Tsukuba, Japan (suburban)	µg/l	2.5	18	n/a
	Huston et al. (2009)	Brisbane, Australia (urban)	µg/l	2.0 ± 0.9	16.4 ± 10.1	2.1 ± 0.7
	Bringmark et al. (2013)	Eight European countries	mg/m <sup>2</sup> /yr	0.5 – 3.0	1.4 - 20	0.5 – 2.4
	Garnaud et al. (1999)	Paris, France (urban)	µg/l	6.0	38.8	13.7
		Fontainebleau, France (urban)		2.2	40.0	2.5
		Chatou, France (suburban)		3.0	34.1	13.5
		Créteil, France (suburban)		7.2	29.8	10.5
<i>Dry</i>	Sansalone and Ying (2008)	Louisiana, U.S. (urban)				
		particulate	µg/l	88.7 ± 16	737.5 ± 193	72.1 ± 6.1
		dissolved		11.1 ± 6.7	88.6 ± 48.7	1.7 ± 1.8
	Wong et al. (2003)	Pearl River Delta, China (mix)	mg/m <sup>2</sup> /yr	18.6	12.7	104
	Paode et al. (1998)	Chicago, U.S. ( <sup>a</sup> urban, <sup>b</sup> near-urban, & <sup>c</sup> rural)	mg/m <sup>2</sup> /d	0.06 <sup>a</sup>	0.2 <sup>a</sup>	0.07 <sup>a</sup>
				0.01 <sup>b</sup>	0.01 <sup>b</sup>	0.003 <sup>b</sup>
				0.007 <sup>c</sup>	0.004 <sup>c</sup>	0.004 <sup>c</sup>
	Sabin et al. (2005)	Los Angeles, U.S. (urban)	mg/m <sup>2</sup> /yr	3.2	13	0.04



## **2.3. Regulations**

### **2.3.1.      *Stormwater regulations***

Traditionally, the emphasis on urban stormwater planning and design has been on water quantity controls, particularly in flooding prevention and downstream erosion alleviation (Chen and Adams 2006). Nowadays, with an array of legislation protecting urban waterways, interest in stormwater quality management has increased (Zoppou 2001). For example, the United States, adopted the National Pollutant Discharge Elimination System (NPDES) under the Clean Water Act, 33 U.S.C. 1251 et seq. (1972). The NPDES regulates point sources that discharge pollutants into waterways (U.S. EPA 2009). The European Union implemented the Water Framework Directive (WFD), Directive 2000/60/EC; its objective is to protect, enhance, and restore water bodies to a good chemical and ecological status by 2015 (European Commission 2014). In New Zealand, the Resource Management Act (RMA), implemented in 1991, is the primary piece of legislation regulating stormwater discharges. Its purpose is to “promote the sustainable management of natural and physical resources” (RMA 1991). One of the primary principals of “sustainable management” is to avoid, remedy, or mitigate any negative environmental effects. In addition, for the Canterbury Region, New Zealand, the Canterbury Regional Policy Statement (CRPS) was implemented in 2013. Its purpose is to set out the “objectives, policies, and methods” to deal with resource management issues and to attain the integrated management of physical and natural resources of Canterbury (CRPS 2013). For the management of water resources, regional councils have the function to control “the discharge of contaminants... into water, and discharge of water into water” (CRPS 2013). Additionally, the CRPS incorporates the fundamental principles of water management detailed in the Canterbury Water Management Strategy (CWMS). The CWMS was developed by Environment Canterbury (ECan), Ngāi Tahu, Canterbury Mayoral Forum, territorial authorities, industry, stakeholders, and non-governmental organisations to address Canterbury’s water management issues using an integrated management approach (ECan 2011).

The “Canterbury Natural Resources Regional Plan (NRRP)” was composed by Environment Canterbury (ECan) to aid the implementation of the several functions set out in the RMA and CRPS (NRRP 2009). It is the regions principal environmental planning framework for sustainably managing water quality and quantity. It also provides the resource consenting requirements for stormwater discharges under Regional Rules WQL1 & 8. The NRRP employs the ANZECC (2001) guidelines that established guidelines for the maintenance and enhancement of the “ecological integrity” of marine and freshwater ecosystems. The guidelines provide pollutant thresholds, including those in stormwater, for the protection of aquatic ecosystems. The thresholds are derived trigger values for toxicants, which if not exceeded a percentage of the aquatic species in a freshwater ecosystem will be protected. Christchurch typically employs the ANZECC 90% protection level.

### **2.3.2.      *Atmospheric pollution regulations***

The National Environmental Standards for Air Quality 2004 (NES) is the main piece of legislation on air quality, made under the RMA 1991. The regulation set standards, which prohibit activities that emit significant quantities of dioxins and other toxics (including heavy metals) into the atmosphere (Ministry for the Environment 2011). Furthermore, the regulations set limits for allowable levels of pollutants in the atmosphere for: carbon monoxide, nitrogen dioxide, ozone, sulphur dioxide, and PM<sub>10</sub>. The NRRP provides additional information on the air quality issues related to the Canterbury and guidance on managing air quality for the Canterbury region.

# Chapter Three: Materials and Methods

### **3. MATERIALS AND METHODS**

#### **3.1. Rationale for Methodology Employed**

The methodology employed in this research, i.e., analysing atmospheric pollutant loads in stormwater runoff from modular paving slab systems, had been successfully demonstrated by Wicke et al. (2010). There are other methods that have been employed for monitoring atmospheric pollutants in stormwater, for example, grease plates, Owen gauges, and aerosol samplers (see Table 3-1). However, most of these methods do not quantify atmospheric deposition onto typical urban surfaces accurately (Lin et al. 1993). Furthermore, not all of the deposited particles collected by these other techniques will realistically be washed-off from urban surfaces; some pollutant fractions will be resuspended by wind, or be sequestered by the impermeable surface (due to entrapment, accretion, adsorption and other means) (Sabin et al. 2005). These other methods cannot accurately measure the quantity of atmospheric pollutants that are resuspended and sequestered by pavement surfaces, and therefore, cannot give a true representation of the total quantities of atmospheric pollutants in stormwater runoff. However, the methodology employed in this research takes atmospheric pollutant build-up and wash-off characteristics of pavement surfaces into account. In particular, this methodology can consider pollutant build-up trends, i.e. the asymptotic increase of pollutant loads with antecedent dry days (Gunawardena et al. 2011; Wicke et al. 2012a). Therefore, quantifying the contribution of atmospheric deposition in urban runoff by employing this methodology will more closely align with actual environmental dynamics. In addition, this methodology can be implemented to include simultaneous setups of different pavement types (impermeable and permeable pavements) and materials (concrete and asphalt).

Unlike the experiments of Wicke et al. (2010, 2012a, & 2012b) that used simulated rainfall in their research, natural rainfall was used to monitor pollutant wash-off here. Using natural rainfall enabled the pollutant loads in wet deposition to be included when monitoring atmospheric fallout fluxes. As both wet and dry deposition influence the atmospheric deposition flux, it is prudent to include both deposition forms into pollutant loading estimates (Mijić et al. 2010). However, this methodology has some disadvantages: meteorological

variables governing pollutant build-up and wash-off (e.g. rain depth) cannot be controlled and only a small sample set with suitable rainfall conditions can be obtained.

**Table 3-1 Types of samplers used to monitor the contribution of the atmospheric deposition in stormwater.**

<b>Sampler used in study</b>	<b>Author</b>
<i>Total Deposition Collector</i>	Davis and Birch (2011)
<i>Aerosol Sampler</i>	Sansalone and Ying (2008)
<i>Grease Plates</i>	Sabin et al. (2005) & (2006)
<i>Owen Gauge</i>	Lamprea and Ruban (2008) & (2011)
<i>Dual Dry and Wet Deposition Sampler</i>	Garnaud et al. (1999)
	Gunawardena et al. (2011) & (2013)

### **3.2. Experimental Components**

To answer the research aims and objectives identified in Section 1.3.1, this research was divided into three experimental components:

*Component 1: What effect do different land-use activities and meteorological variables have on airborne pollutant build-up and wash-off (research question iii and iv)?*

To answer these research questions, modular impermeable concrete boards were deployed in three land-use areas (industrial, residential, and airside) within Christchurch, New Zealand, from February 2013 to December 2013. The boards were deployed in each land-use areas for one year so that changes to atmospherically derived pollutant loads in stormwater could be analysed against various meteorological conditions. Impermeable concrete was selected over asphalt because concrete has a greater resistance to extreme temperatures, unlike asphalt that tended to distort in its framework when exposed to high temperatures ( $\geq 25^{\circ}\text{C}$ ). As the boards were exposed to the elements for almost one year, concrete was the preferred choice as its performance could be guaranteed throughout the duration of the study.

*Component 2: How much does wet deposition contribute to the total atmospheric deposition flux? What is the relationship between pollutant loads in wet deposition and atmospheric particulate matter concentrations (research question v)?*

This experimental component involved analysing wet deposition samples for Cu, Pb, Zn, and turbidity from August 2013 to March 2014. Wet deposition samples were collected in the industrial land-use area only. The pollutant loads in wet deposition were analysed against atmospheric particulate matter concentrations to ascertain any relationships between them. In addition, pollutant loads in wet deposition were compared to the pollutant loads in runoff from the impermeable concrete boards at the industrial sampling site (component 1), so that the contribution of wet deposition to the total atmospheric deposition flux could be analysed.

*Component 3: What effect do different impermeable and permeable pavements have on retaining atmospheric pollutants (research question i and ii)?*

For this experimental component<sup>2</sup>, the effects of pavement type (i.e. pavement composition and surface roughness) on airborne pollutant runoff/infiltrate was analysed from June 2014 to August 2014 at the residential sampling site only. The pavement types studied were impermeable asphalt, permeable asphalt, impermeable concrete, and permeable concrete. Additionally, pollutant loads in wet deposition and bulk deposition were measured and compared to the pollutant loads in runoff/infiltrate from each pavement type.

### **3.3. Impermeable Paving Slab System**

The impermeable paving slab system was designed to simulate atmospheric pollutant wash-off from two typical urban surfaces: asphalt (component 3) and concrete (component 1 and 3). It comprised of an impermeable modular paving slab (from here on referred to as a board), a Dexion frame, and a stormwater collection system. Atmospheric pollutants were deposited on the board during antecedent dry days, which subsequently during rainfall, were mobilised and transported via surface runoff to the stormwater collection system.

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<sup>2</sup> Note: for clarity proposes and ease of reading, the results of component 3 are represented in the first thesis result chapter (Chapter 4).

### **3.3.1.      *Impermeable concrete boards***

The concrete pavements (Con) were constructed using the concrete mix in Table 3-2. Approximately 0.018 m<sup>3</sup> of concrete were used to fill a board's framework. Once filled, the boards were placed on a vibrating table for a minute to homogenise the concrete mix. The concrete had a thickness of 18 mm; therefore, to reinforce the thin concrete board, plastic fibres were added to the concrete mix. After the concrete was poured into its framework, the concrete was kept hydrated for seven days to prevent cracking during the drying process. The concrete was then allowed to cure for an additionally 21 days. Following this, the concrete boards were removed from their frameworks. A diamond bladed grinder was used to remove a thin surface layer off the concrete to obtain a smooth even surface. Any pollutants that had built up on the boards during the construction stage were removed using a high-pressure washer.

The concrete boards were subjected to natural weathering/erosion processes during the course of experimentation, in particular, to acidic rain. However, Kanazu et al. (2001) found that the erosion depth of concrete with a water/cement ratio of 60% (corresponding to the concrete used in this research) was below 0.1 mm after applying 2,500 mm of rainfall at pH 5.6. As it is atypical for Christchurch rainfall to have a pH<5.6 and as the total rainfall volume over the course of this research was approximately 760 mm, the erosion depth of the concrete was minimal; therefore, was not of a concern. Additional corrosion processes, i.e., artificial physical (e.g. traffic) or chemical (e.g. chlorides from deicing salts) forces were not applied.

**Table 3-2 Impermeable concrete recipe for one board - equivalent to 0.018 m<sup>3</sup> of concrete.**

<b>Material</b>	<b>Quantity</b>
Cement	6.3 kg
Tap water	3.75 l
13 mm aggregate	22.5 kg
Sand	20.25 kg
Shogun (plastic) fibres	0.225 kg
Sika (polymer) megafibres	0.0225 kg
Water reducer (Plastiment RMC01, Sika Ltd.)	20.25 ml

### **3.3.2. *Impermeable asphalt boards***

The impermeable asphalt<sup>3</sup> (Asp) used in this research was obtained from a supply of material used to construct a local carpark; therefore, as the asphalt was not made specifically for this research, the results were representative of a newly constructed carpark. The hot mix ‘virgin’ asphalt, composed of 10 mm maximum aggregate and Grade 80-100 bitumen (NZ Transport Agency 2011). The asphalt was compacted into the framework using a plate compactor to obtain a surface composition similar to typical carpark surfaces. The depth of the asphalt was 32 mm; this exceeded the recommended minimum asphalt depth requirement (2.5 times the maximum aggregate size) (J. Forrest, Fulton Hogan, personal communication, February 25, 2013). Additionally, the depth ensured a uniform surface, with minimal voids, that was analogous to carpark surfaces. The asphalt cured for two days before prepping for experimentation. Unlike the concrete boards, the framework was not removed from the asphalt, due to concerns over its rigidity during high temperature days.

### **3.3.3. *Impermeable asphalt and concrete board design***

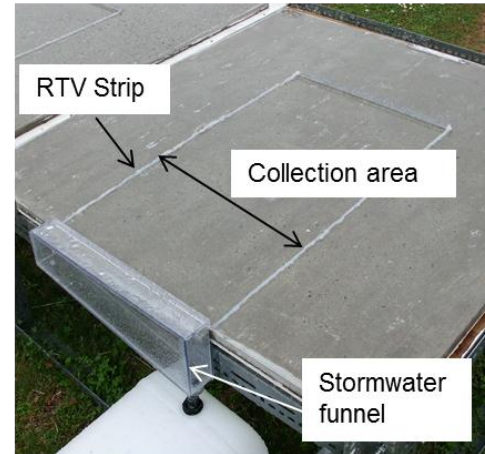
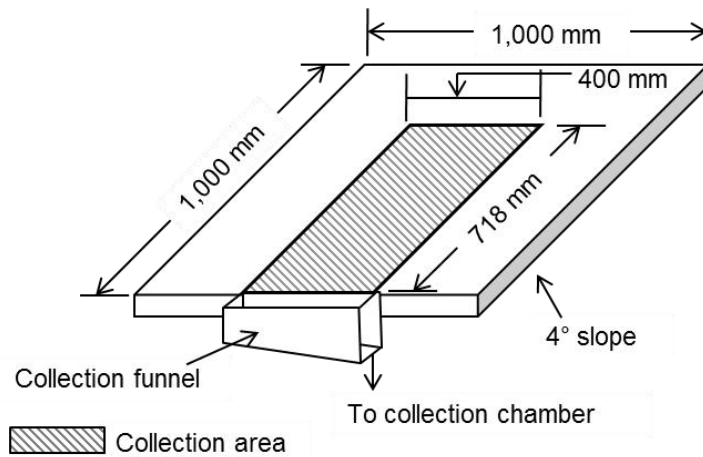
The impermeable boards had a surface footprint of 1.00072 m<sup>2</sup>, as exemplified in Figure 3-1. A collection area, where the runoff was solely collected from, was incorporated into the board

<sup>3</sup> The asphalt boards were constructed with the assistance of Fulton Hogan Construction.



design (Figure 3-1) to account for pollutant loss due to splash and spray. That is, during a rain event, pollutants can be mobilised and carried off the board via splash/spray; thus, resulting in inaccurate pollutant concentrations being reported. By including a collection area into the board design, it was assumed that the splash/spray leaving the collection area would equal the splash/spray entering into it from the remainder of the board. The distance between the edges of the collection area to the edge of the board (300 mm) was chosen after a preliminary experiment on splash and spray was conducted. The experiment found that the majority of splash traversed <250 mm from its point of origin. To account for wind and experimental error this distance was extended to 300 mm.

The collection area was defined using a 3 mm high strip of Room Temperature Vulcanising Silicone (RTV). Additionally, at the top of the collection area, a strip of polycarbonate (15 mm in height) was attached to the board to prevent any runoff entering into the collection area. However, due to the potential of runoff flowing over the RTV strip as it approached the collection system, an additional strip of RTV (5 mm high) was placed halfway down the collection area. In conjunction, a polyvinyl chloride (PVC) strip (40 mm x 15 mm) was attached to the side of the RTV strip and the collection system to prevent runoff leaking around the sides of the collection system. Furthermore, the collection area protruded into the funnel; thus, ensuring all the runoff was collected. This is exemplified in Figure 3-2. The height of the RTV strip was chosen to minimise any disruption to the wind flow over the board, while ensuring no loss of runoff from the collection area. Maintaining the flow of wind over the board was essential for pollutant resuspension into the atmosphere, which more closely aligned to the natural environment.



**Figure 3-1 Top view of an impermeable board.**



**Figure 3-2 A RTV strip and a plastic piece used to channel runoff into the stormwater collection system.**

#### *3.3.3.1. Preliminary experiment of splash and spray*

To determine the extent of splash and spray, a high-speed camera (Panasonic HDC-SD900) captured images of simulated rain landing on an impermeable concrete and asphalt board in a precursory laboratory experiment. The rain (average intensity - 12.4 mm/h) was generated using a two nozzle (Veerjet 80100) Norton type rainfall simulator. The energy of the

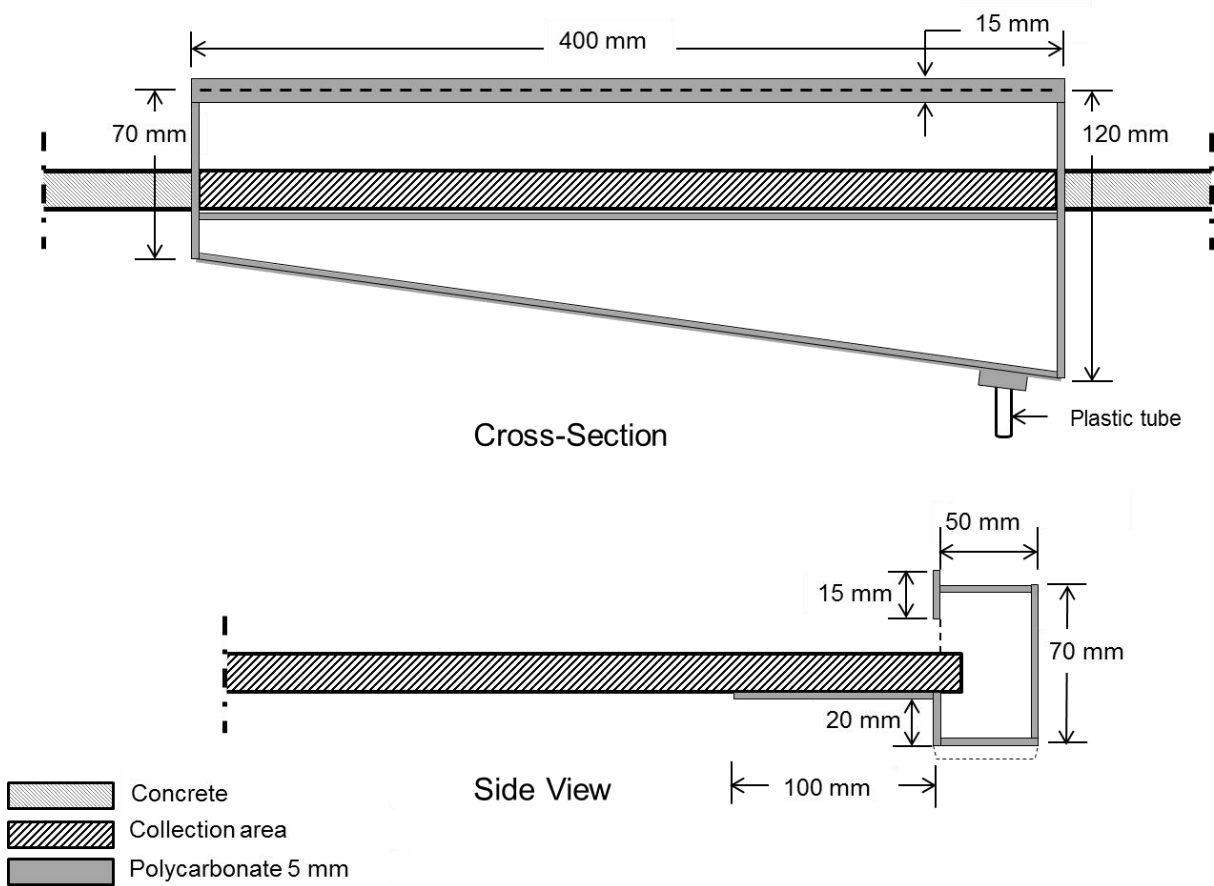
raindrops (200 kJ/ha-mm) equated to natural rainfall of 10 mm/hr intensity (95% of Christchurch rain events are below 10 mm/h) (Meyer and Harmon 1979). Rain splash with a trajectory perpendicular to the camera was monitored and the distance evaluated. For both the impermeable asphalt and concrete boards the majority of splash travelled within 25 cm from its point of generation; however, some splash exceeded 40 cm. This methodology for monitoring rain splash had some limitations: firstly, errors occurred when measuring the distances of splash from a three-dimensional environment in a two-dimensional image; secondly, rain splash would likely travel farther with the influence of wind in the environment; and thirdly, splash generated from a heavier rain intensity event would have larger trajectories. Pollutant losses due to rain splash could not have been mitigated, but it was minimised with the inclusion of a collection area into the board design.

#### **3.3.4. *Dexion frame***

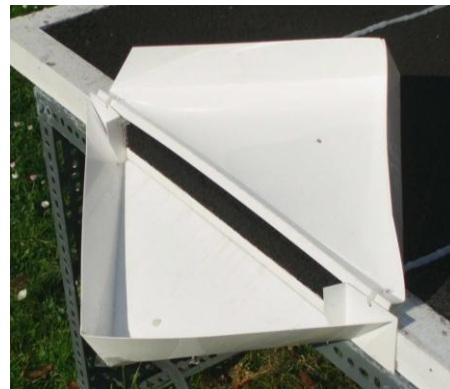
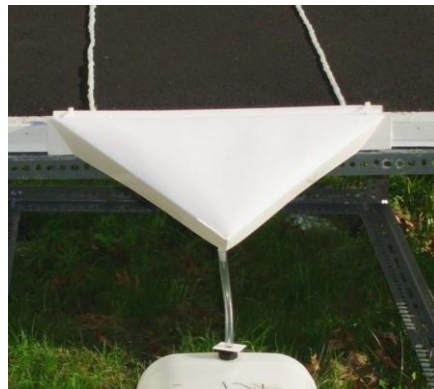
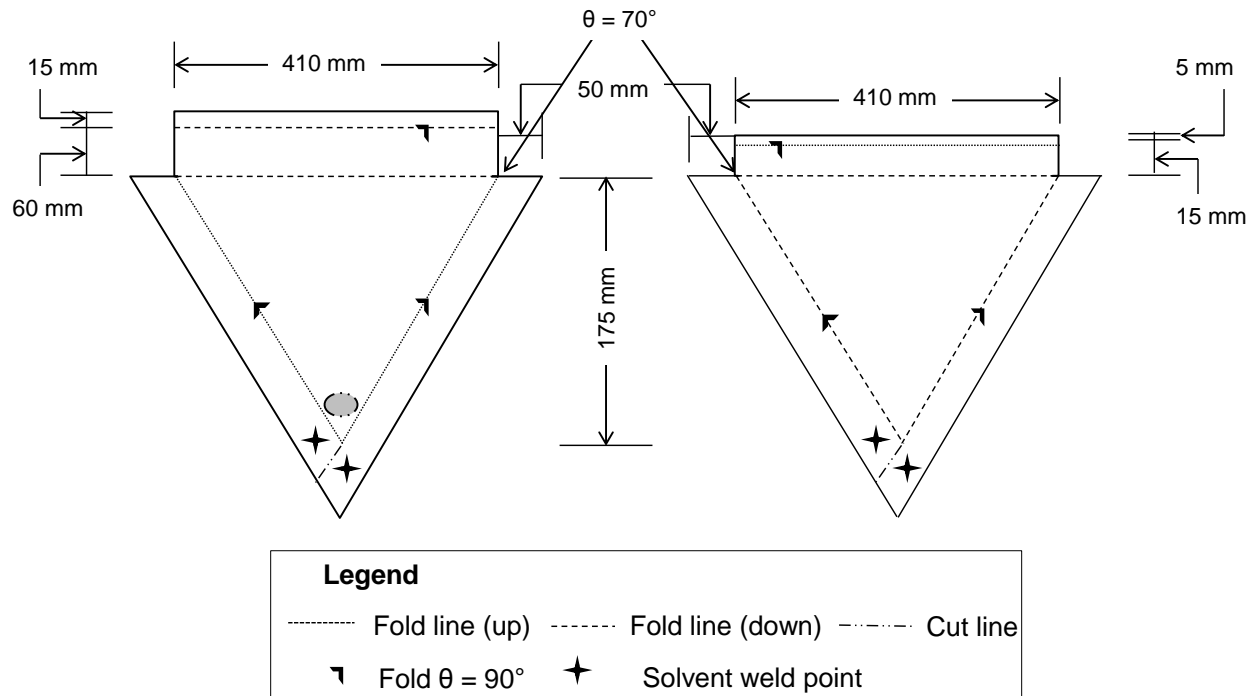
The boards were elevated from the ground (approximately 0.5 m) by a Dexion frame. The Dexion was galvanised and painted to prevent rusting of the frames during its course in the field. The frames inclined the boards at  $4^{\circ} \pm 0.1^{\circ}$  from the horizontal. The heights of the Dexion frame were altered using adjustable feet to enable the  $4^{\circ}$  slope to be accurately obtained.

#### **3.3.5. *Stormwater collection system***

The stormwater collection system contained two parts: a collection funnel and a 20 L High Density Polyethylene (HDPE) collection chamber. The funnel collected stormwater from the collection area and quickly released it into the collection chamber. The funnel for the concrete boards was constructed using polycarbonate due to its strength and its good ultraviolet resistance (Figure 3-3). For a minimal stormwater retention time, the funnel had an angle of  $7.1^{\circ}$ . However, as the funnel displayed a weakness along the glue joints, the funnel was redesigned for the asphalt boards. The funnel was instead constructed using 2 mm thick PVC; the shape was created by bending and solvent welding the PVC (Figure 3-4).



**Figure 3-3 Side and top view of the stormwater collection funnel for the concrete boards.**



**Figure 3-4 Development of the bottom (left) and the top (right) section of the stormwater collection system for the impermeable asphalt boards.**

### 3.4. Permeable Paving Slab System

Two types of permeable pavement systems were studied in this research (component 3): porous asphalt (OGPA) and permeable concrete (PCon). Modular interlocking concrete bricks with external/internal drainage cells (MICBEC and MICBIC) were excluded from this research because the properties of asphalt and concrete on pollutant wash-off were of primary interest. As this research was only concerned with the removal of TSS and heavy metals, only

the top layer of the permeable pavement system was studied. The top layer of the permeable pavement system behaves like a filter for pollutants and is responsible for the removal of TSS and heavy metals (Abustan et al. 2012; Dierkes et al. 2002; Dierkes et al. 1999). In addition, in New Zealand and the U.S. for example, a top layer of OGPA is occasionally employed over an impermeable roading surface as a road safety measure. Thus, this study also aimed to quantify pollutant attenuation (if any) by the OGPA layer when incorporated into the road design.

#### **3.4.1. *Permeable paving slab system design***

The permeable paving slab system (here on referred to as a permeable board) had a surface footprint of approximately  $2.86 \times 10^5 \text{ mm}^2$ , which corresponds to the footprint of the collection area on the impermeable boards. Unlike the impermeable boards, the permeable boards did not have an area included for splash and spray because splash/spray from the permeable boards was minimal. The permeable boards had a depth of 50 mm. Typically in New Zealand, the depth of a OGPA layer does not exceed 40 mm (J. Forrest, personal communication, February 10, 2014); for a PCon layer, the depth is rarely below 100 mm (A. Scott, personal communication, February 15, 2014). As this research was concerned with comparing the properties (e.g. chemical composition) of OGPA and PCon, a consistent depth between the boards was of greater importance than mimicking the depths used in practical applications. The depth of 50 mm was chosen as it was between the depths typically used for permeable asphalt/concrete and it minimised the weight of the boards.

##### **3.4.1.1. *Permeable concrete boards***

The PCon was constructed using the concrete mix described in Table 3-3;  $0.014 \text{ m}^3$  of concrete was use to fill one board's framework. Once filled, the concrete was lightly compacted to level the surface. The concrete was left to cure for three days before being removed from its framework. Once removed, the concrete was left to cure for an additional 21 days. Throughout the curing process, the permeable concrete was kept hydrated to prevent

structural failure. Vacuum suction and a high-pressure washer were used to remove any pollutants that built up in the PCon void spaces during construction. Surface runoff from the PCon was not expected because rainwater infiltration through the PCon was instant.

**Table 3-3 Permeable concrete recipe for one board - equivalent to 0.014 m<sup>3</sup> of concrete.**

<b>Material</b>	<b>Quantity</b>
Cement	4.97 kg
Tap water	1.59 l
6-9 mm aggregate	21.56 g

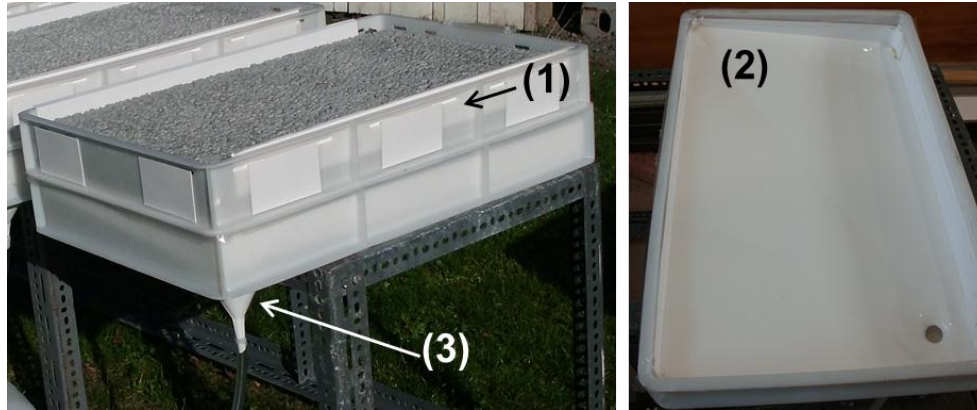
#### *3.4.1.2. Porous asphalt boards*

The hot mix ‘virgin’ OGPA<sup>4</sup> composed of maximum 10 mm aggregate and Grade 80-100 bitumen (NZ Transport Agency 2011), which corresponded to what is typically used on roads. The asphalt was compacted into the framework using a plate compactor to obtain an even surface. The OGPA was released from its framework after two days of curing. Vacuum suction and a high-pressure washer removed any pollutants trapped in the OGPA’s voids during construction. Surface runoff from the OGPA was not expected because rainwater infiltration was instant.

#### **3.4.2. Stormwater collection system**

The stormwater collection system was designed to capture the infiltrate from the permeable pavement boards. The collection system comprised of four parts (Figure 3-5): (1) a mesh nylon tray to support the permeable pavement board; (2) a PVC funnel (with the same dimensions as the tray); (3) a tray structure to hold the funnel in place and to support the permeable pavement board above the funnel; and (4) a HDPE collection chamber. Infiltrate was funneled into a HDPE collection chamber where it was held until collection.

<sup>4</sup> Constructed with the assistance of Fulton Hogan Construction.



**Figure 3-5 The permeable paver stormwater collection system. Where (1) is a nylon support tray for the PCon (2) is a PVC funnel; and (3) is a supporting structure for the PVC funnel and the PCon.**

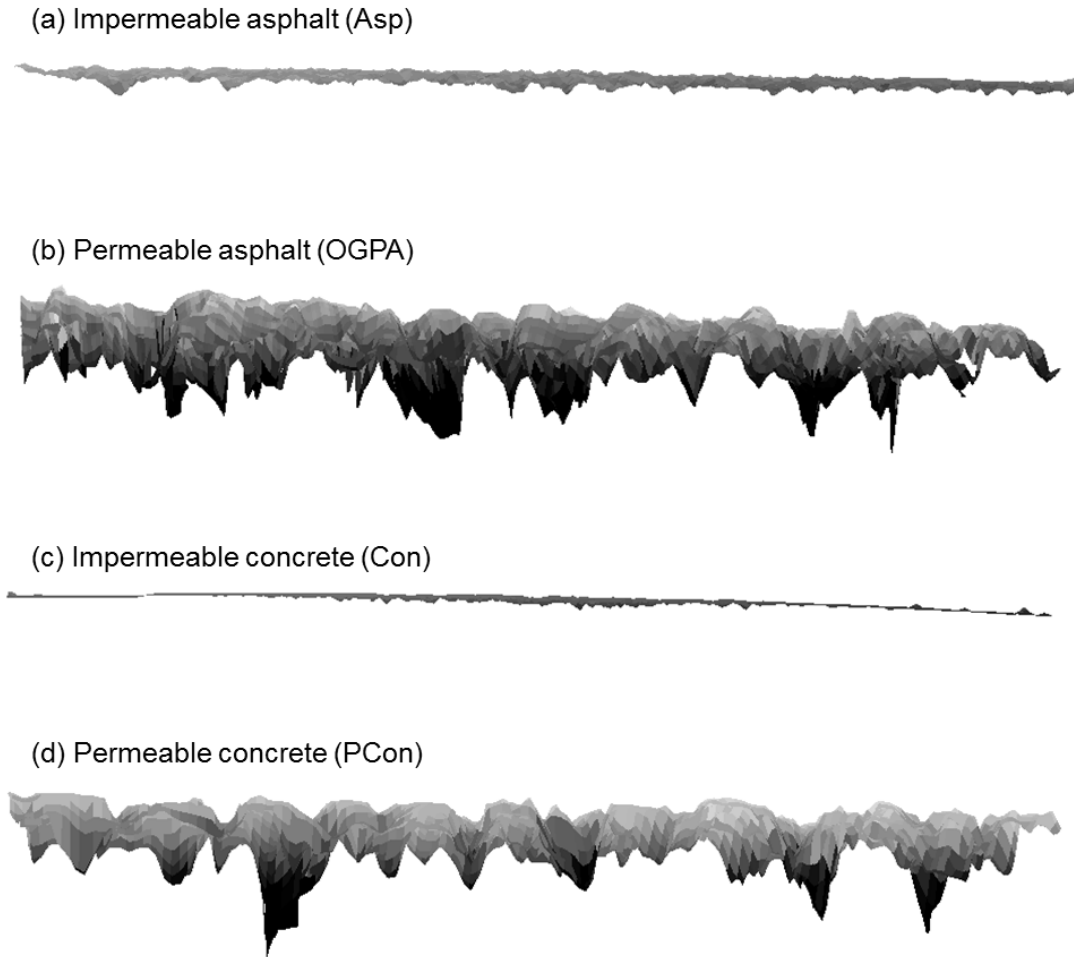
### **3.5. Surface Roughness Properties of the Pavement Types**

The surface roughness of the impermeable and permeable boards were assessed using an Instantaneous-Profile Laser Scanner as detailed in Darboux and Huang (2003). The laser scanner was calibrated according to the manufacture's guidelines (Bramer 2007). Elevation matrices were analysed in ArcGIS 10.2 (ESRI 2013). Images of the surface topography are exemplified in Figure 3-6. Surface roughness was determined from the minimum and maximum elevation in relation to the mean planar layer of the board. Standard deviations (S.D.) of surface elevation were used to quantify the surface roughness characteristics (Table 3-4). The permeable boards had a rougher surface composition than that of their impermeable counterparts. The impermeable concrete boards had the smoothest surface. The permeable concrete had the roughest surface, which was associated with the large voids spaces in the pavement structure.

**Table 3-4 Surface roughness characteristics from the different pavement types.**

<b>Pavement type</b>	<b>Mean (mm)</b>	<b>Min. (mm)</b>	<b>Max. (mm)</b>	<b>S.D. (mm)</b>
Con	8.69	8.26	8.90	0.09
Asp	11.31	10.89	11.58	0.11
OGPA	11.63	10.69	12.16	0.14
PCon	11.89	10.82	12.23	0.15





**Figure 3-6 Laser scanned vertically exaggerated topographical images of each pavement type.**

### **3.6. Background pollution from the pavement boards**

Prior to deploying the pavement boards to the field, the initial pollutant background levels from the boards were monitored. A rainfall simulator (as described in Section 3.3.3.1) was used to simulate rainfall for background pollutant wash-off. The feed water used to simulate rainfall was passed through a 10  $\mu\text{m}$  filter to remove any solid particles. A control sample of the feed water was taken and analysed for heavy metals, turbidity, and alkalinity; the results were taken into account during data analyses of the wash-off samples. The pH of the feed water was approximately seven, which was higher than the rainfall pH in Christchurch (4.9 –

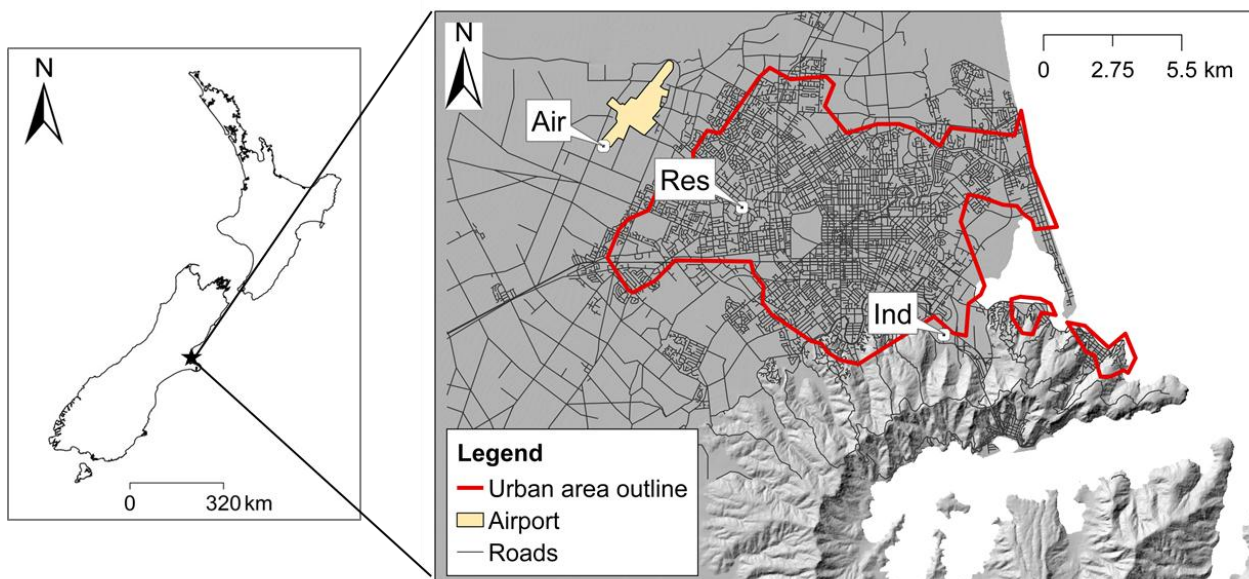
7.2) (Wicke et al. 2014); therefore, dissolved Cu, Zn and Pb wash-off during the sampling campaign would have been higher because lower pH increases the solubility of metals. To account for this, only total metals were analysed when monitoring background pollutant loads. Prior to sample collection, the boards were flushed with simulated rainfall with a rain intensity of 120 mm/h for 5 minutes. The rain intensity was then reduced to 10 mm/h and the wash-off was collected over a period of 30 minutes. Results on the pavements background pollutant levels are discussed in Section 4.3.1 and 5.3.1..

### **3.7. Sample Locations**

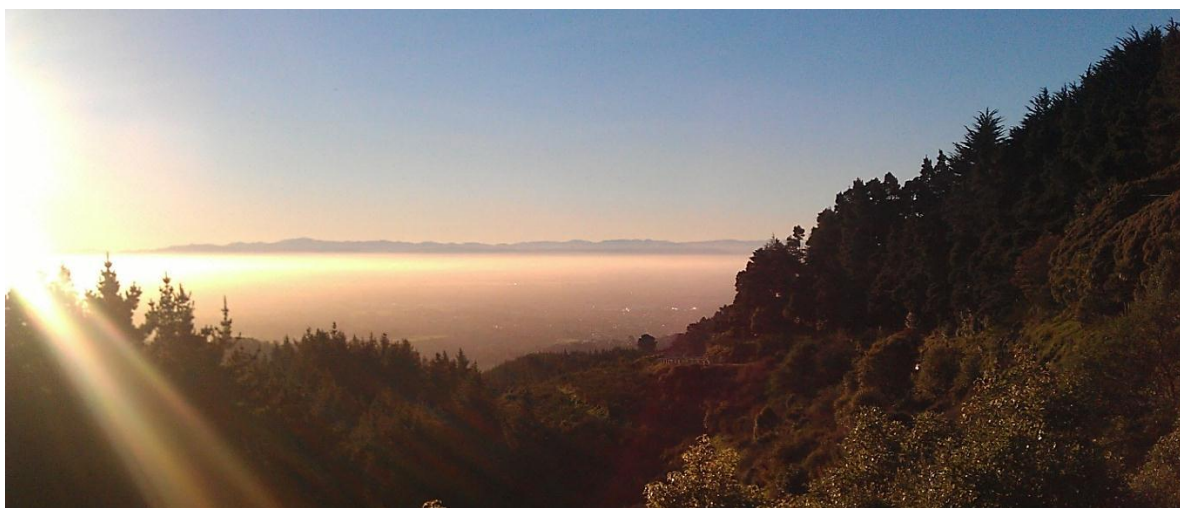
Three study sites (industrial, residential, and airside) were selected to assess the spatial and temporal distribution of atmospherically derived pollutants in stormwater in Christchurch (component 1), the third most populous city in New Zealand (land area  $\approx 1,500 \text{ km}^2$ ; population  $\approx 341,500$ ) and the largest city in the South Island (Figure 3-7). Christchurch is located on the coastal edge of the Canterbury Plains, east of the Southern Alps. A remnant volcano (Banks Peninsula) lies to the south of Christchurch. The climate of Christchurch is semi-arid, which is associated with long antecedent dry periods and low rainfall, northeasterly winds prevail for much of the year; however, southwesterlies are common in winter. Christchurch is prone to smog events (Figure 3-8) that typically occur during cold calm nights when the emissions from domestic heating are high and the atmosphere is stable (Kossmann and Sturman 2004). Smog events are a principal result of the strong near-surface temperature inversions during anticyclonic synoptic conditions (Sturman et al. 2011). Two main rivers run through Christchurch City, the Avon/Ötakaro and Heathcote/Opawaho rivers. Both the rivers run through heavily urbanised areas of the city and receive stormwater drainage from a variety of sources, which ultimately ends up in the Avon-Heathcote Estuary/Ihutai (ECan 2007). The estuary itself is of major importance - it hosts an abundance of wildlife and it is of great cultural and historical importance to the local Maori.

The industrial (Ind) land-use area comprised of light industry; in the immediate vicinity, there was a holding yard for shipping containers, a liquid petroleum gas depot, retail premises, and

warehouses. No high-temperature industrial processes occurred near the Ind sampling site. The residential (Res) land-use area had approximately 2,046 dwellings (typically detached dwellings) within a radius of 1 km, and a housing density of approximately 651.6 dwellings/km<sup>2</sup> (data derived from ArcGIS (ESRI 2013)). The airside site (Air) was within Christchurch International Airport, which is the second largest airport in New Zealand, servicing approximately 5,500 airplane movements per month (international and domestic). The airport has two runways: the main runway (northeast to southwest) operates on a 24-hour basis and is capable of handling Code E size aircrafts (e.g. Boeing 777). The secondary runway (northwest to southeast) is predominately used in a northwesterly wind, which occurs mainly in spring (southern hemisphere) when much of the northwest conditions occur; the use of this runway is limited to aircraft of Code D and smaller (e.g. Boeing B767). The airside and residential areas had similar topography – flat land with no nearby hills or mountains surrounding the sites. The industrial site was located next to a hill range (Port Hills) with two spurs on either side of the site (Figure 3-7). The concrete boards at the Ind site were orientated at a 215° heading to face away from the building that could interfere with pollutant dispersal. The orientation of the concrete boards in Air was at a 45° heading to face the primary runway and the prevailing wind (northeasterly). All boards (impermeable/permeable concrete and asphalt) at Res were positioned at a 45° heading to face the prevailing wind (northeasterly).



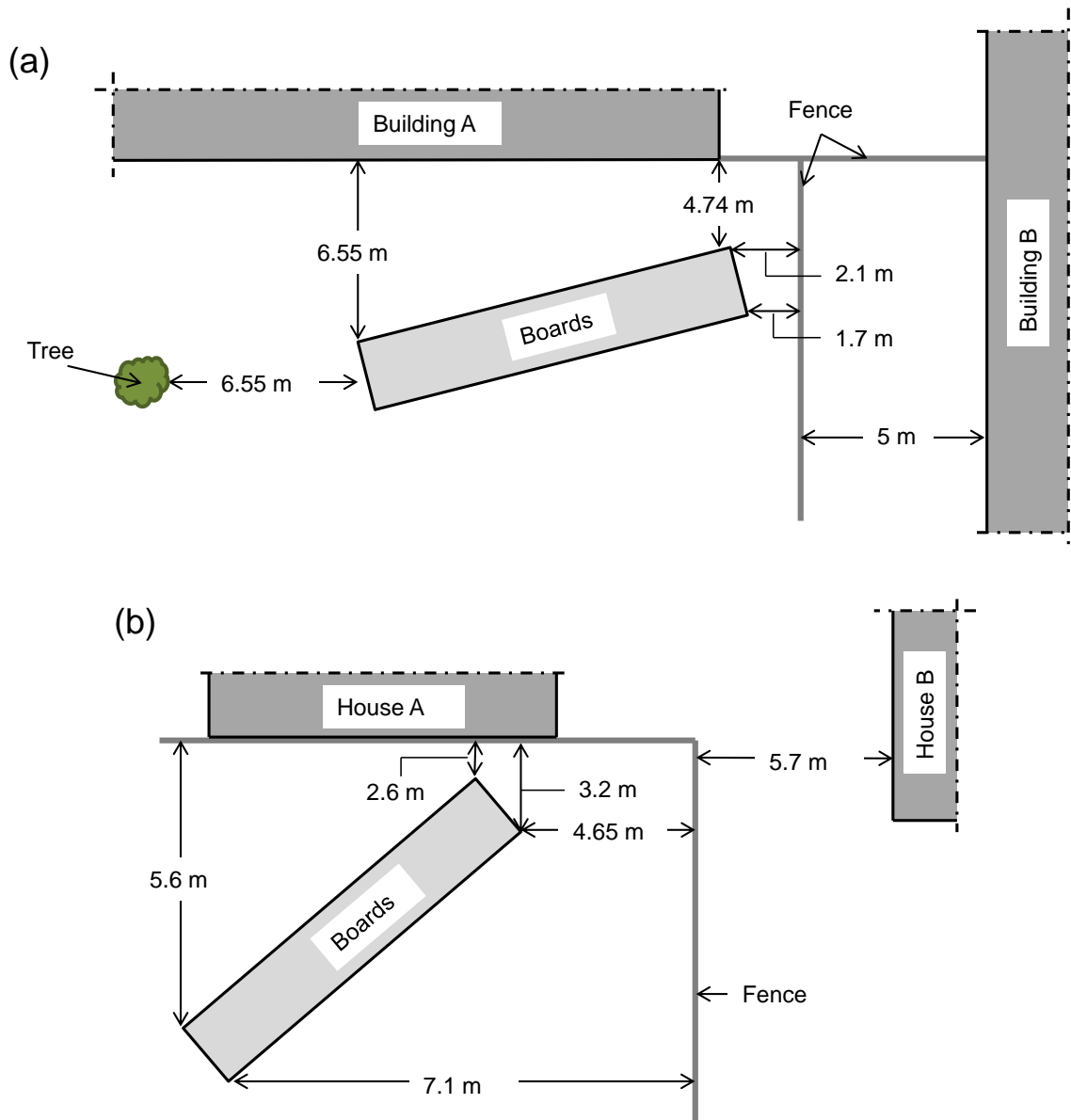
**Figure 3-7 Air (S43 30.063 E172 31.222), Res (S43 31.390 E172 35.290), and Ind (S43 34.145 E172 41.252) monitoring sites in Christchurch, New Zealand.**



**Figure 3-8 Smog over Christchurch City.**

Neighbouring buildings, as shown in Figure 3-9, surrounded the experimental setup at the Res and Ind testing sites. This was unavoidable because these catchments are densely populated and obtaining a secure testing area with no surrounding structures was unattainable. However,

pavements are typically surrounded by structures in these catchments; therefore, these testing sites represented what was frequently seen in an industrial and residential land-use area.



**Figure 3-9 The distance between the concrete boards and the neighbouring buildings on (a) Ind and (b) Res (a) Buildings A and B are three stories high; (b) Houses A and B are two stories high.**

### 3.8. Sampling Procedure

After a rain event, stormwater (runoff and infiltrate) was captured and collected within 24 hours of the start of the event. However, this was not always possible, i.e. when the rain event lasted all day and concluded at night, the samples could not be collected until the morning for safety reasons. Before collecting the samples, the collection chambers were weighed to obtain the runoff volume. Although the boards were alike, there were variances in the runoff volumes from the boards, even in the same site. After establishing rain gauges around the experimental setups, it was found that the rainfall depth varied between each board. Within distances of 4 m, a difference of 0.5 mm rain depth was observed; therefore, the effects of wind and rain shadow had a prominent effect on runoff volumes. To account for the variances in runoff volumes from the boards, pollutant loads were analysed rather than concentration, as concentration would have been affected by the increased runoff, i.e. the dilution effect.

All stormwater samples were homogenised in-situ prior to sub-sampling into headspace free HDPE sampling bottles. All samples were stored below 4°C and transported to the University of Canterbury for analyses (see Section 3.9). The collection chambers were rinsed twice with deionised water to remove any residual particles before being reconnected to the collection funnel.

To monitor pollutant loading as a function of weather conditions (component 1) (Section 3.2), the concrete boards were intensely washed between experimental runs. Residual pollutants remaining (i.e. the fixed load) on the boards were removed via brushing (Vaze and Chiew 2002) and flushing with deionised water after each rain event. The OGPA, PCon, Con, and Asp pavement boards (component 3) were not washed after a rainfall event, so the influence of pavement type on retaining pollutants during varying rainfall events could be monitored.

### 3.8.1. *Weather data*

The meteorological parameters of principle concern were rainfall and wind patterns. Details on the weather instruments measuring these parameters are in Table 3-5. Different instruments were used to measure wind and rainfall at the three experimental research sites due to equipment availability. However, the accuracy of each instrument used was within an acceptable range, and thus, the measured weather parameters were consistent between the experimental research sites. Wind data for Ind and Air were obtained in 10-minute intervals. The wind data was averaged to the hour using equations 3-1 to 3-4 modified from Stull (1995):

$$U = - M * \sin(\alpha) \quad \text{eq. 3-1}$$

$$V = - M * \cos(\alpha) \quad \text{eq. 3-2}$$

*Average U and V into hourly intervals for  $U_{(av)}$  and  $V_{(av)}$*

$$\text{Average speed} = [(U_{(av)})^2 + (V_{(av)})^2]^{1/2} \quad \text{eq. 3-3}$$

$$\text{Average direction} = 90^\circ - (180^\circ / \pi) * \arctan (V_{(av)} / U_{(av)}) + x \quad \text{eq. 3-4}$$

Where, wind speed = M (m/s) and direction =  $\alpha$  (radians),  $x = 180^\circ$  when  $U_{(av)} > 0$ , or  $x = 0^\circ$  when  $U_{(av)} \leq 0$ .

**Table 3-5 Information regarding the collection of weather data.**

	<b>Parameter</b>	<b>Weather station</b>	<b>Instrument type</b>	<b>Accuracy</b>	<b>Distance from testing area</b>
Air	Rainfall	Local rain gauge	Davis tipping bucket	±4% (intensity <50 mm/h) ±5% (intensity >50 mm/h)	On-site
	Wind	Local wind sensor	RainWise Wind-Log	Speed: ± 2% Direction: ± 22.5°	On-site
Ind	Rainfall	Local rain gauge	Davis tipping bucket	±4% (intensity <50 mm/h) ±5% (intensity >50 mm/h)	On-site
	Wind	ECan air monitoring station	Vector Instruments W200P & A100M	Speed: ± 1% Direction: ± 3°	1.44 km
Res	Rainfall	UC weather station	Rain-O-Matic Professional	± 2%	0.45 km
	Wind	NIWA weather station	Vector Instruments W200P & A100M	Speed: ± 1% Direction: ± 3°	1.77 km

### 3.8.2. *Comparison with past weather conditions*

Rainfall during the months that research occurred was compared to the average monthly rainfall from the previous 10 years (Table 3-6). February and March 2013 were drier than the average and had long antecedent dry periods. However, April to June 2013 had greater rainfall depths than the average from the previous 10 years. July and August 2013 had slightly lower rainfall than the average, but September to December 2013 had similar rainfall depths than that of the previous 10 years. Therefore, the year 2013 (component one of the research) was an atypically year of rainfall in Christchurch. Thus, the year sampled may not have been representative of “normal” weather in Christchurch. However, the results were still used as they enabled a wide range of weather parameters to be measured in this study (e.g. long antecedent dry periods). Component two of the research was conducted from August 2013 to



March 2014. January and February of 2014 were characterised by lower than average rainfall. March 2014, on the other hand, had a large amount of rainfall, which occurred within a short period. Component three of the research was conducted in a period that had similar rainfall to the 10-year average, with the exception of August, which had lower rainfall amounts. Therefore, component two and three of the research was conducted during times of typical rainfall amounts in Christchurch; however, with the exception of a few atypical months, which could not have been avoided.

**Table 3-6 Monthly rainfall amounts (mm) during each research component compared to the average monthly rainfall from the previous 10 years (mean  $\pm$  S.E.). Where “-” represents months where no research was conducted; blue colour represents months of atypical low rainfall; and red colour represents months of atypical high rainfall.**

Month	2003 – 2012 average	2013	2014
<i>Jan</i>	32.48 $\pm$ 4.61	-	17.2
<i>Feb</i>	44.10 $\pm$ 9.65	20.4	28.4
<i>Mar</i>	38.24 $\pm$ 4.64	22	213.6
<i>Apr</i>	48.20 $\pm$ 5.65	62.2	-
<i>May</i>	77.25 $\pm$ 16.84	127.2	-
<i>Jun</i>	56.26 $\pm$ 12.16	220.4	68
<i>Jul</i>	60.44 $\pm$ 10.55	49.4	43.4
<i>Aug</i>	82.46 $\pm$ 15.80	44.4	17.8
<i>Sep</i>	31.80 $\pm$ 6.31	31.8	-
<i>Oct</i>	55.98 $\pm$ 8.74	54.4	-
<i>Nov</i>	35.32 $\pm$ 6.31	29.2	-
<i>Dec</i>	59.34 $\pm$ 13.16	65.2	-

### 3.8.3. *PM monitoring*

Particulate matter  $<10 \mu\text{m}$  and  $<2.5 \mu\text{m}$  ( $\text{PM}_{10}$  &  $\text{PM}_{2.5}$ ) data was obtained from the Environment Canterbury (ECan) air-monitoring station in the industrial area of Woolston, Christchurch (S43 33.431 E172 40.868). PM concentrations were monitored 1.44 km away from the Ind testing site. PM concentrations were monitored and analysed by ECan. QA/QC protocols were implemented by ECan. However, data following 19 November 2013 had not

yet been audited by ECan. Therefore, analyses on PM concentrations were conducted with the unaudited data because the data was unlikely to vary significantly after the audit is conducted.

#### **3.8.4.      *Wet deposition sampling***

A wet deposition sampler (WDS) was deployed at the ECan air-monitoring site where PM was measured (component 2) and outside the University of Canterbury's Environmental Lab (component 3) (Figure 3-10). The WDS was deployed in those locations because they were protected from public interference and had access to a power supply. Additionally, the pollutant loads from wet deposition (component 2) could be compared directly to the PM data monitored at the ECan air-monitoring site. The WDS (N-Con ADS Model 00-120-2) had an infrared transmitter and receiver that opened the sampler within 20 seconds of the onset of precipitation and closed it within a minute of precipitation finishing. The capacity of the polyethylene-sampling container in the WDS was 13.25 L. Wet deposition samples were collected within 24 hours of the rain event concluding. The samples were analysed for Cu, Zn, Pb, and turbidity; TSS was not analysed, as the sample volumes were insufficient for analyses.



**Figure 3-10 Wet deposition sampler deployed at the Woolston air monitoring station - the center of the industrial catchment.**

#### **3.8.5. *Bulk deposition sampling***

Bulk deposition samples (combination of dry and wet deposition) were collected outside the University of Canterbury's Environmental Lab (component 3). Bulk deposition samples were collected in a 13.25 L polyethylene container. The container was exposed to both dry and wet deposition. After a rain event, the bulk deposition sample was analysed for Cu, Zn, Pb, and turbidity; TSS was not analysed, as the sample volumes were insufficient for analyses. The bulk deposition sample represented the maximum deposition that occurred on all the pavement types before pollutant resuspension by wind action and pollutant sequestering by the pavement material.

### **3.9. Analytical Analysis**

Depending on the volume of runoff collected, different analytical parameters were examined (Table 3-8). As a minimum, heavy metals and turbidity (TSS surrogate) had to be monitored, as heavy metals and suspended solids were of principle concern in this research. If sufficient

sample was available, TSS was analysed for each board in conjunction with heavy metals and turbidity. Since turbidity is caused by suspended solids, turbidity was used as a surrogate for TSS when the runoff volumes were too low for analyses. A regression equation for the relationship between turbidity and TSS was developed for component one of the research (influence of land-use area and meteorology), as shown in Table 3-8. TSS loads from bulk deposition loads (component three – influence of pavement type) were estimated by applying the turbidity concentrations from bulk deposition into a TSS-turbidity relationship curve ( $\ln(\text{TSS}) = 0.955 \cdot \ln(\text{turbidity}) + 0.9008$ ). The curve ( $R^2 = 0.765$ ) was generated using the turbidity and TSS concentrations from the Con boards as it was assumed that the deposited particulates loads would not be sequestered by the pavement; therefore, representing BD better. However, with further examination (see Section 4.3.3.3), this assumption was proved to be erroneous.

**Table 3-7 Component 1 (spatial and temporal variations) prediction models for TSS.**

<b>Location</b>	<b>Model</b>	<b>R<sup>2</sup></b>	<b>Sig.</b>
<i>Air</i>	$\ln(\text{TSS}) = 0.994 \cdot \ln(\text{turbidity}) + 0.930$	0.857	<0.001
<i>Res</i>	$\ln(\text{TSS}) = 1.031 \cdot \ln(\text{turbidity}) + 0.908$	0.732	<0.001
<i>Ind</i>	$\ln(\text{TSS}) = 0.89 \cdot \ln(\text{turbidity}) + 1.709$	0.815	<0.001

Other parameters (pH, alkalinity, and conductivity) were only analysed if there was excess sample remaining. As pH, alkalinity, and conductivity were not of principle concern, it was deemed acceptable that these analytical parameter were not consistently monitored throughout the research. For small rain events with insufficient sample for heavy metal and turbidity analyses (<0.6 mm/h), the sample was not collected. Instead, the sample was left in the collection chamber and collected after the next rain event. The total antecedent dry period of the subsequent rain event was taken as the sum of the two antecedent dry periods (dry period before and after the small rain event). This was deemed appropriate, as it was assumed that the rainfall volume during these small rain events was insufficient to remove the pollutant load built-up during the antecedent dry period; therefore, the combined antecedent dry period was representative of the true pollutant build-up.

**Table 3-8 Parameters that were analysed after a rain event of certain depth and the minimum runoff volume required for analyses.**

<b>Rain depth (mm)</b>	<b>Min. volume needed (L)</b>	<b>Parameters to be analysed</b>
1	0.15	Total/dissolved metals and turbidity
1.8	0.4	Total/dissolved metals, turbidity, conductivity, and pH
1.8 – 3.2	0.8	Total/dissolved metals, turbidity, conductivity, pH, and alkalinity
4.0	1.15	Total/dissolved metals, turbidity, and TSS*
4.6	1.4	Total/dissolved metals, turbidity, TSS, conductivity, and pH
5.3	1.8	Total/dissolved metals, turbidity, TSS, conductivity, pH, and alkalinity

\*Conductivity and pH were not analysed in this instance, as analysing TSS from the limited runoff was deemed more important. Additionally, using the same sample to analyses pH, TSS, and conductivity was deemed inappropriate as cross-contamination may occur.

### **3.9.1. pH**

pH was measured *in situ* using a pH meter (YSI 60). The meter was calibrated prior to each experimental run with fresh 4.0, 7.0, and 10.0 S.U. buffers in accordance with the manufacturer's guidelines. Calibrations were checked after sampling to ensure the accuracy of the measurements. The pH of stormwater in component 3 (pavement type) was analysed using an EDT RE357Tx Microprocessor because the stormwater samples could be analysed more accurately, but without breaching the maximum holding times. The pH meter was calibrated prior to analyses with fresh 4.0, 7.0, and 10.0 S.U. buffers in accordance with the manufacturer's guidelines.

### **3.9.2. Alkalinity**

Alkalinity was analysed in accordance to SM2340 (APHA 2005) using the potentiometric titration curve method. The pH meter (EDT RE357Tx Microprocessor) was used to measure changes to pH.

### **3.9.3.      *Specific conductivity***

Specific conductivity was measured using the YSI 30 conductivity meter. The meter was maintained and calibrated following the manufacturer's guidelines. Calibration of the instrument occurred prior to sampling using a standard of 0.01 M KCl (1412  $\mu\text{S}/\text{cm}$  at 25°C).

### **3.9.4.      *Turbidity and total suspended solids***

The turbidity meter (Hach Model 2100P) was calibrated with freshly prepared formazin standards (0, 20, 100 and 800 NTU). Calibrations were checked prior to sampling with a 0-10 NTU range, 0-100 NTU range, and 0-1000 NTU range Gelex secondary turbidity standards. TSS and turbidity were measured within 48 hours in accordance with SM2540-D (APHA 2005).

### **3.9.5.      *Heavy metals***

Total recoverable metal (Cu, Pb, Zn) samples were preserved with concentrated  $\text{HNO}_3$  (70% Fisher, trace analysis grade) to a  $\text{pH} < 2.0$  (APHA 2005). The total recoverable metal digestions were prepared by mixing 25 ml of homogenised sample with 5 ml of  $\text{HNO}_3$  into a 50 ml polypropylene centrifuge; the mixture was boiled for one hour in a heating block and allowed to cool. The cooled samples were filtered through an encapsulated 0.45  $\mu\text{m}$  polyvinylidene difluoride (PVDF) filter (47 mm, Labserv) before ICP-MS analysis (Wicke et al. 2012b; Good 2011). Dissolved metal samples were filtered through a 0.45  $\mu\text{m}$  PVDF filter before being preserved with  $\text{HNO}_3$  to a  $\text{pH} < 2.0$ . All heavy metals were analysed by ICP-MS (Agilent) according to SM3125-B (APHA 2005).

### 3.9.6. *Quality control and quality assurance*

All samples were collected, preserved, and analysed following the APHA (2005) guidelines. To minimise any errors in the data acquisition, a quality assurance (QA) and quality control (QC) plan was implemented. In compliance with the QA/QC plan, at least 10% of the samples were duplicated. Duplicates were analysed via the APHA (2005) relative percent difference (RPD) equation 3-5:

$$RPD = \frac{S - D}{\frac{S + D}{2}} \times 100\% \quad \text{eq. 3-5}$$

Where: S = sample result and D = duplicate result

When duplicate values exceeded 10% of the sample result, the instrument was recalibrated (if required) and the samples re-analysed. Standards and blanks were carried out regularly. Spiked samples from a matrix-matched calibration standard were used to verify the heavy metal analyses (ICP-MS). The certified reference material used for heavy metal analyses was NIST (seawater). All instruments were calibrated and maintained according to the manufacturer's manual. All samples were analysed within the maximum holding time (the time between collection and analyses) and preserved in accordance to the APHA (2005) guidelines (Table 3-9). All results reported were above their detection limits. The detection limit for Cu and Pb was 1 µg/l; the detection limit for Zn was 10 µg/l; the detection limit for TSS was 3 mg/l. Any data that was below the detection limit (principally dissolved Pb) was discarded.

All sampling equipment was acid washed with 10% HCl for a minimum of seven days and rinsed three times with ultrapure deionised water. All the stormwater collection systems and collection chambers were initially decontaminated before deployment in the field by soaking in 10% HCl for >24 hours to remove any residual heavy metals acquired during their construction.

**Table 3-9 Preservation methods and maximum holding times (APHA 2005).**

Analytical parameter	Preservation & storage	Maximum holding time
pH	-	Immediately
Alkalinity	4°C	14 days
Conductivity	4°C	28 days
Turbidity and TSS	4°C	48 hours
Total & Dissolved Metals	HNO <sub>3</sub> < pH 2	6 months

### **3.10. Statistical Analysis**

Statistics were conducted using the IBM SPSS Statistics 20 and the R 3.0.2 packages. All dependent variables were transformed (log) to comply with the assumptions of linearity and normality (Field 2013). Where required, linearity and normality were confirmed using scatterplots and Q-Q plots. Homogeneity of variance was confirmed using the Levene's test (Field 2013). Any significant outliers were removed from the data set to avoid bias (Field 2013).

#### **3.10.1. MANOVA and effect-size analyses**

A one-way multivariate analysis of variance (MANOVA) test was performed to ascertain whether statistical differences existed between independent groups on more than one continuous dependent variable. Differences between the continuous dependent variables were analysed by *post hoc* Gabriel analysis for its superior capabilities at handling unequal sample sizes (Field 2013). Assumptions of normality and homogeneity of variance were confirmed prior to analyses. Where the MANOVA test failed the homogeneity of variance assumption, a permutation MANOVA test was conducted, followed by multiple ANOVA's (Gabriel adjusted).

When MANOVA analysis was not suitable, i.e., when there is a combination of a small sample size and a big effect size (such as in Chapter 4) which results in spurious p-values (Coe 2002), statistical difference were analysed using Cohen's *d* effect size (Cohen 1988).



Effect size analysis was conducted because it was a simple way to quantify the difference between groups (Coe 2002). Cohen's  $d$  for within-student designs was calculated using eq. 3-6 (Olejnik and Algina 2000). Values for  $d$  can range from 0 to infinity – the higher the  $d$ -value the greater the effect of the treatment (in this instances, the effect the pavement had on retaining atmospheric pollutant loads). The  $d$ -values are typically categorised into small ( $d = 0.2$ ), moderate ( $d = 0.5$ ), or large ( $d = 0.8$ ) effects; the values are arbitrary but they provide a useful benchmark for novel studies.

$$d = \frac{\psi_1 - \psi_2}{\frac{\delta_1 + \delta_2}{2}} \quad \text{eq. 3-6}$$

Where:  $\psi$  is the population means and  $\delta$  is the standard deviation of the populations.

### **3.10.2.      *Bivariate correlation***

A bivariate Pearson's correlations were conducted between the dependent and independent variables to ascertain if any relationships existed. Pearson's correlation is a measure of the strength of a linear association between an independent and dependent variable and is denoted by  $r$ . The values for  $r$  can range from -1 to 1; a value of 0 indicates that there is no relationship between the variables studied (Field 2013). Assumptions of normality and linearity were confirmed prior to Pearson's correlation analyses.

### **3.10.3.      *Mixed effect modelling***

Mixed effects models (a form of regression analyses) were used to develop a prediction model between a dependent variable and multiple independent variables while accounting for a random effect. Cross-validation techniques were employed to find the simplest, most parsimonious mixed-effect model. More details on mixed effect models are provided in Chapter 6.

#### **3.10.4.     *Principle component analysis***

Principle component analysis (PCA) was used to define the variation within the dependent or independent variable groups. PCA uses orthogonal transformations to convert a set of correlated variables into a set of linearly uncorrelated variables called principal components (Field 2013). Each principle component explains a set amount of variance in the original data. The number of components extracted was established by the Kaiser's criterion (Kaiser 1960). The Kaiser-Meyer-Olkin measure of sampling adequacy ( $KMO > 0.5$ ) was validated prior to conducting the PCA test (Kaiser 1974).

# Chapter Four:

## The Influence of Different Pavement Types on Atmospheric Pollutant Attenuation and Wash-Off

## **4. THE INFLUENCE OF DIFFERENT PAVEMENT TYPES ON ATMOSPHERIC POLLUTANT ATTENUATION AND WASH-OFF**

### **4.1. Introduction**

Road are one of the most prevalent types of impermeable surfaces (Arnold and Gibbons 1996). The total length of roads in New Zealand is 94,160 km, in which local roads make up 83,244 km and state highways make up 10,916 km (Ministry of Transport 2014). Approximately 62,760 km of the road network is sealed (Ministry of Transport 2014). Roads can be constructed with either asphalt or concrete materials, although, asphalt is more commonly used. Approximately 90% of the 5.2 million km of roads and highways in Europe are paved with asphalt; in the U.S., approximately 92% of the 4 million km of roads and highways are paved with asphalt; in Canada, about 90% of the 415,000 km of roads are paved with asphalt (NAPA & EAPA 2011). In New Zealand, roads are principally constructed with asphalt.

Increased government spending on road infrastructure (primarily for state highways) was announced in the 2009 Government Policy Statement for Land Transport (revised version). From 2009-2019, the government will invest \$NZ 10.7 billion in state highways via the Roads of National Significance (RoNS) programme (New Zealand Government 2010). Therefore, a vast amount of pavement material will be generated. The type of pavement material used, permeable or impermeable, concrete or asphalt, will influence pollutant build-up and wash-off dynamics feeding into stormwater runoff. This presents an opportunity to choose the best pavement type for attenuating airborne (and other) pollutants in runoff.

#### **4.1.1. *Asphalt pavements***

Asphalt contains a mixture of coarse aggregate, filler (sand or stone dust), and bitumen<sup>5</sup> (Lindgren 1996). Bitumen, when liquefied at high temperatures, is the binder that

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<sup>5</sup> Bitumen here refers to the binder and asphalt refers to the mixture of the bitumen binder and mineral aggregate.

amalgamates the aggregate together (called hot mix asphalt) (Roberts et al. 1996). The ratio of aggregate to bitumen varies depending on the strength and durability requirements of the road, but most frequently a ratio of 95% aggregate to 5% bitumen is employed (Lindgren 1996). The aggregate for asphalt is usually obtained from local supplies of natural rock (Roberts et al. 1996). Bitumen is a by-product from the fractional distillation of crude oil. It comprises of long-chained hydrocarbons with high vaporisation temperatures that remain after the smaller, lighter molecules in crude oil have been refined off during the fractional distillation process (Whiteoak 1990). Following fractional distillation, the bitumen undergoes further distillation at a reduced pressure to form a 'short residue'. This short residue is further altered by air blowing to increase the amount of asphaltenes in the bitumen and to increase the asphaltenes' molecular size (Whiteoak 1990). Asphaltenes are the viscosity-building component of the bitumen. The bitumen contains principally hydrocarbons, followed by a small quantity of sulphur, nitrogen, and oxygen. Heavy metals, such as nickel and vanadium, are present in trace quantities (Roberts et al. 1996). Zinc is rarely present in road bitumen (Kennedy and Gadd 2000). However, a detailed characterisation on the chemical structure of the bitumen is difficult to obtain because of its complexity (Lindgren 1996). This is further complicated because the chemical composition of the bitumen will vary according to the crude oil source and the modifications applied to it (Lindgren 1996; Roberts et al. 1996). Therefore, no two asphalt pavements will have identical chemical compositions.

#### **4.1.2.        *Concrete pavements***

A concrete pavement consists of cement (typically Portland cement), coarse aggregate (commonly gravel or crushed stone), fine aggregate (sand), water, and chemical admixtures (Bernot et al. 2011). Portland cement is a binder for the aggregates and is composed of calcium aluminates, calcium aluminoferrites, calcium silicates and gypsum (Bernot et al. 2011). Portland cement is made by heating a mixture of limestone (the calcareous material) and clay (the silica and alumina material) to approximately 1,500°C to produce a 'clinker' (John 2003). The clinker, once cooled, is finely ground and blended with gypsum to prevent flash-setting of the cement (John 2003). Frequently other materials, such as fly ash and blast

furnace slag, are added to the cement mix (John 2003). When water is added to the cement, the silicates and aluminates form hydrates, which produce a firm hard mass, i.e. the hardened cement paste (Neville and Brooks 2010).

#### **4.1.3.      *Impermeable concrete versus impermeable asphalt roads***

Asphalt is the most widely used pavement material in the world because it is cheaper and faster to make than concrete, which requires high initial investment and long curing times (Portland Cement Association and National Asphalt Pavement Association 1986). Although, the initial cost of concrete is greater than asphalt, research states that over its life cycle, concrete roads are a cheaper alternative to asphalt (Stroombergen 2013). However, a life cycle assessment into the energy consumption of concrete versus asphalt states that because asphalt can be readily recycled, it was more sustainable (environmental burden factors calculated on economic sector levels) over its lifetime (Horvath and Hendrickson 1998). In addition, utilising recycled asphalt for materials can result in a significant reduction in costs compared to constructing a pavement with all virgin material (Portland Cement Association and National Asphalt Pavement Association 1986). Although, both concrete and asphalt roads have the capability to be recycled, concrete recycling occurs in smaller quantities compared to asphalt (Horvath and Hendrickson 1998) because virgin aggregate is inexpensive, leaving little incentive to recycle old concrete for aggregate (John 2003). However, choosing to use concrete over asphalt for paving has some environmental benefits, such as increased surface albedo, decreased vehicle fuel consumption, carbon sequestering, and durability (CCANZ 2013). The lighter coloured concrete has a greater surface albedo than a darker asphalt road which reduces the impacts of urban heat islands and direct radiative forcing (CCANZ 2013). Higher reflectivity of the surface requires less lighting demands and it promotes safer driving conditions by enhancing road visibility (Santero et al. 2013). Concrete roads promote lower fuel consumption due the pavements rigidity compared to the flexible asphalt (Zaniewski 1989). Vehicles cause more deflection on flexible pavements, this deflection absorbs some of the vehicles energy which otherwise would have been used to propel the vehicle forwards (rolling resistance) (Zaniewski 1989). Moreover, as concrete roads are smoother than asphalt

roads, vehicle fuel composition is reduced by creating a smoother ride and by reducing friction (Santero et al. 2013). Furthermore, concrete affords some form of carbon sequestering after its construction, called carbonation. Carbonation is at its greatest when the concrete is demolished and broken into fragments, whereby the surface area available to uptake CO<sub>2</sub> is increased. These waste fragments can be recycled into another concrete structure which effectively traps the carbon (Collins 2010). Thus, the concrete can absorb back the CO<sub>2</sub> that was released during its construction. Concrete roads are more durable than asphalt roads, i.e. the service life of concrete is approximately 40 years compared to asphalt which has a service life of approximately 15 years (Portland Cement Association and National Asphalt Pavement Association 1986). Typically, concrete roads are preferred over asphalt roads for areas which are prone to flooding, where the underlying soil is weak, when soil drainage is a major problem, when the aggregates are of low quality, or when the soils are the expansive type (Kanta Rao et al. 2006).

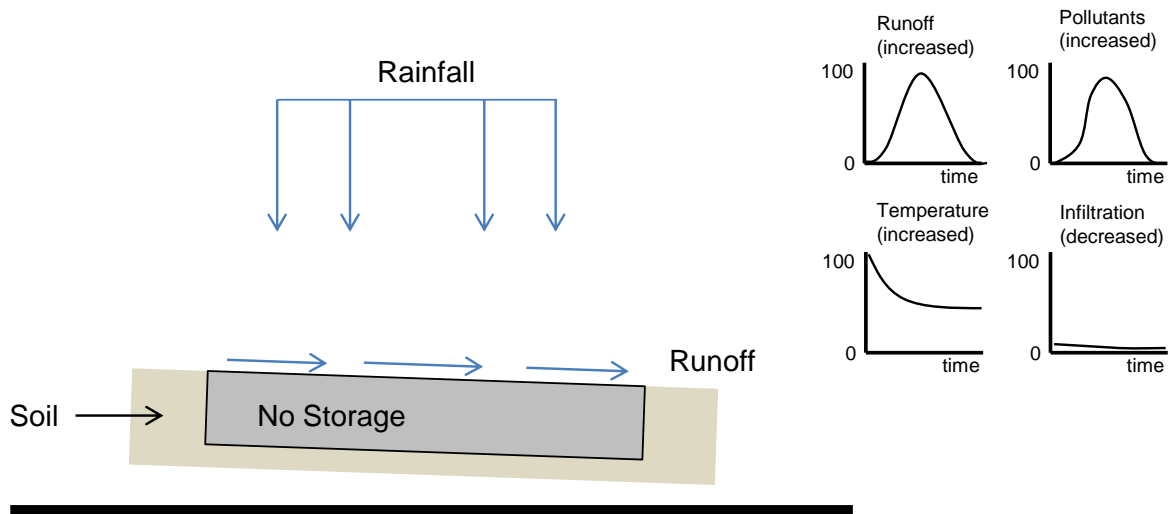
#### ***4.1.4. Permeable pavements***

Permeable pavements are an alternative to the conventional impermeable asphalt and concrete pavements. Permeable pavement systems (PPS) are a type of best management practice (BMP) allowing stormwater to infiltrate through the pavement, rather than running off the pavement as surface flow (Boving et al. 2008). They prevent, or at least delay, runoff generation (Fassman and Blackbourn 2010), and facilitate groundwater recharge (where soil conditions permit) and evaporation (Dierkes et al. 2002), as exemplified in Figure 4-1. Moreover, stormwater infiltrating through the permeable pavers are treated to some extent by filtering out suspended solids and heavy metals (Barrett et al. 2006; Scholz and Grabowiecki 2007). Brattebo and Booth (2003) found that PPS systems reduced concentrations of Cu and Zn in stormwater runoff compared with impermeable systems that provided no treatment. They found that 97% of runoff sampled from impervious pavements exceeded the designated 'toxic' levels for Cu and Zn, but that this was reduced to 14% when PPS were employed. Sansalone et al. (2008) found that permeable concrete reduced stormwater turbidity concentrations by one to two orders of magnitude. Similarly, Legret et al. (1996) found a 64%

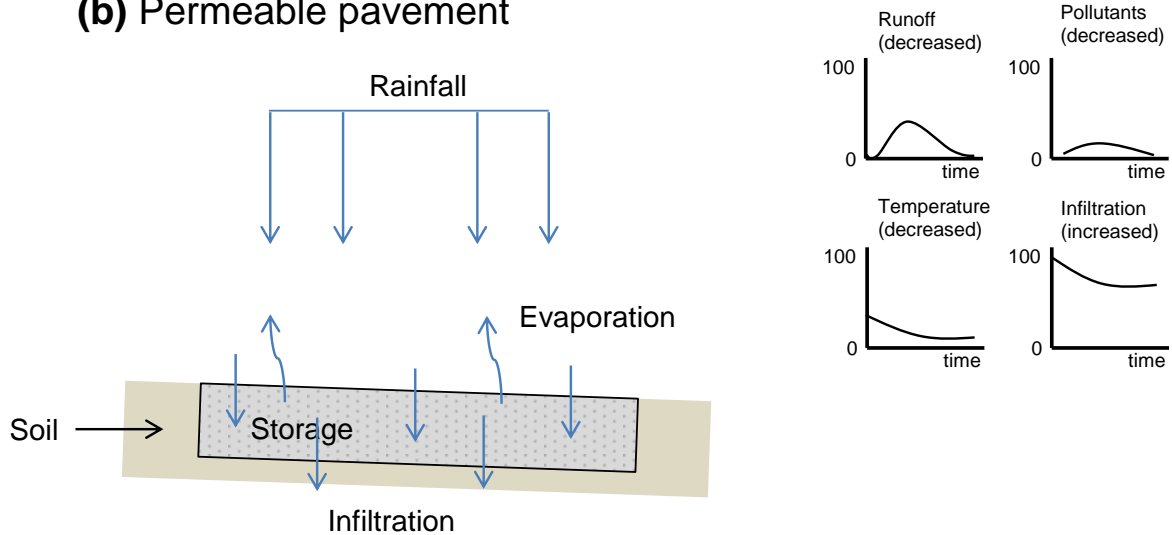
reduction and Stotz and Krauth (1994) found a 50% reduction in TSS concentrations from permeable asphalt compared to a conventional asphalt pavement. Eck et al. (2012) found that in comparison to impermeable asphalt, a permeable friction course (a form of permeable asphalt) reduced TSS, total Cu, total Zn, and total Pb concentrations by 91% - 96%, 56% - 69%, 87%-90%, and >90% - >96%, respectively. Other benefits of PPS include, increased road safety through reduced splash and spray from vehicles, reduced aquaplaning, improved traction, and reduced noise pollution (Barrett 2008). The design principle (Figure 4-2) of PPS is to enable precipitation to infiltrate through to an aggregate-filled basecourse (storage reservoir). Which subsequently can then either exfiltrate through to the subsoil and enter the groundwater system, or be collected by an under-drain (Fassman and Blackburn 2011) and released into a suitable drainage system (Scholz and Grabowiecki 2007).



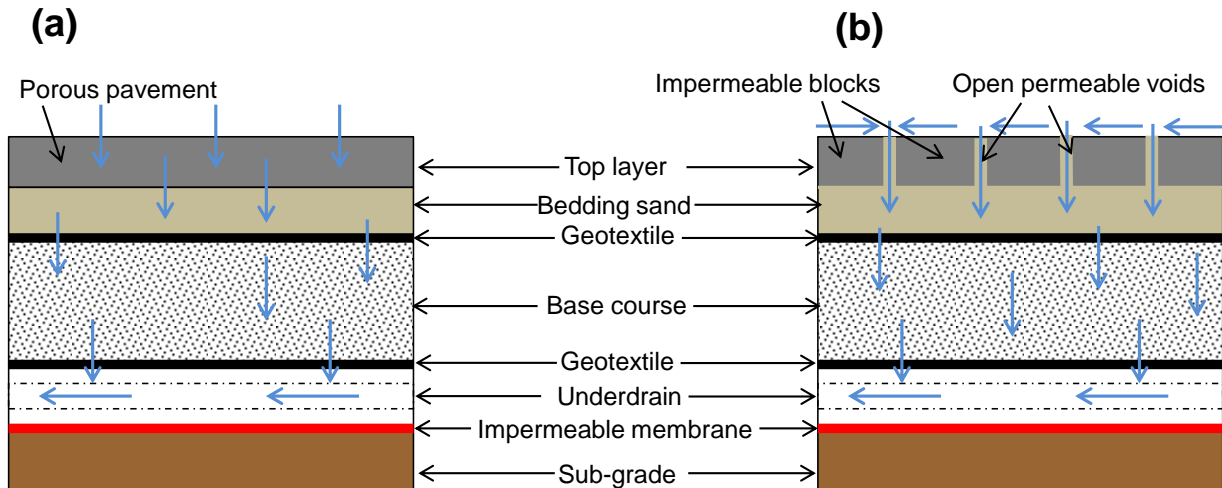
### (a) Conventional pavement



### (b) Permeable pavement

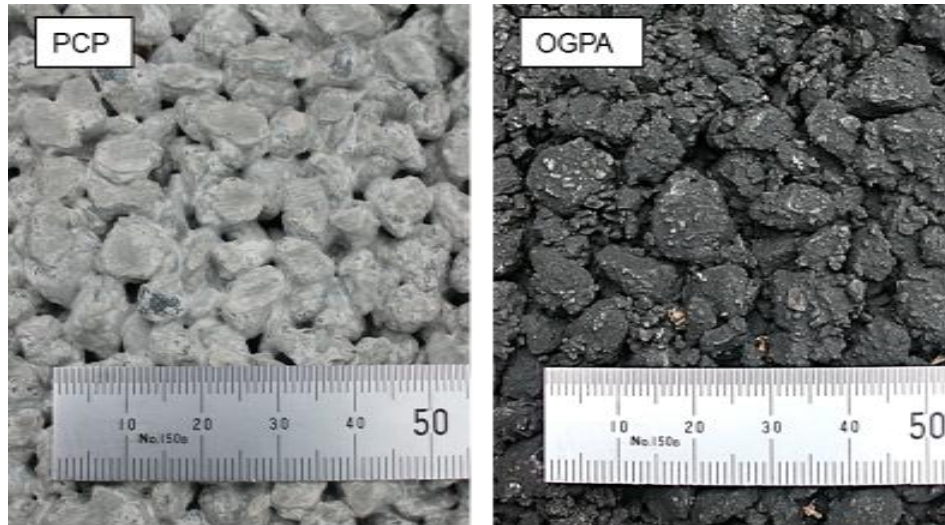


**Figure 4-1 Benefits of (b) permeable pavements over (a) conventional impermeable pavements (modified from Sansalone et al. (2008)).**



**Figure 4-2 Permeable pavement systems design with an underdrain: (a) porous pavement (i.e. Open-Graded Porous Asphalt or Porous Concrete), (b) modular interlocking concrete bricks with external drainage cells. Adapted from (Auckland Council).**

Conventional PPS designs include porous pavers comprising of either Open-Graded Porous Asphalt (OGPA) or Porous Concrete Pavers (PCon) (Figure 4-3 a and b, respectively). OGPA, and PCon are constructed with the omission of fine aggregates (James and von Langsdorff 2003); hence, giving them their porosity and permeability. Alternatively, PPS can be designed using plastic interlocking structures or concrete blocks with voids filled with soil, gravel, or sand (Booth and Leavitt 1999). It is a different treatment strategy to OGPA and PCon, whereby precipitate can only infiltrate through the voids. OGPA is widely used in New Zealand and abroad, especially on urban arterial roads and motorways as a road safety measure rather than a stormwater BMP (Barrett and Shaw 2007; Transit New Zealand 2007). The structural performance of OGPA compared with impermeable asphalt is much lower as the permeable pavement is more prone to rutting (Huber 2000). Similarly, PCon, due to its high porosity, generally has lower durability and strength properties than its traditional impermeable counterpart (Shu et al. 2011). However, under low frequency of usage (e.g. in a carpark) wear of permeable pavements are minor and presents no impediment to its use (Brattebo and Booth 2003).



**Figure 4-3 A PCon and OGPA pavement.**

The primary failure of all PPS's are their susceptibility to surface clogging. Clogging occurs initially with sediment entrapment, then finer particles (e.g., clay particles) become entrapped between the sand grains, which reduces the filtering capacity until eventually an impermeable matrix is formed (Balades et al. 1995). Sediment deposition (from construction works or unstable catchments) is the primary cause of PPS failure; therefore, it is more pragmatic to consider all land use activities in a catchment when evaluating the suitability of installing a PPS (Fassman and Blackbourn 2010). However, clogging is not a major problem as it can be easily solved by street sweeping or flushing (James and Shahin 1998). With adequate maintenance and protection from diffuse sediment inputs such as unmitigated earthworks, the effective life capacity of a PPS is estimated at >20 years (Fletcher et al. 2004). The long-term reduction to the water quality treatment performance of a PPS will occur but it is unlikely to be problematic as the PPS will still be effective at treating stormwater (Brattebo and Booth 2003).

#### ***4.1.1. The influence of pavement composition on pollutant wash-off***

From a stormwater management perspective, not all pavement types are equivalent. In fact, pavement type can impose a strong influence on pollutant wash-off dynamics. Pollutant loads

from pavement runoff are affected by the pavements surface roughness and composition (Wicke et al. 2012b). Surface roughness affects particulate pollutant entrapment and the subsequent capabilities of particulates to be washed-off (Wicke et al. 2012b). For instance, particulate pollutants on a coarse asphalt surface are less likely to be mobilised due to the deeper cavities in the material compared to a smooth (e.g. concrete) surface that enables particulates to be more easily dislodged (Wicke et al. 2012b). Pavement composition affects the movement of pollutants by different physiochemical processes, especially adsorption and desorption, whereby, adsorption describes the adhesion of a pollutant to the surface of a solid and desorption describes the pollutants release (Zoppou 2001). In particular, concrete will have a marked influence on pollutant loads in runoff. Concrete can immobilise dissolved Cu by forming Cu-rich phases on its surface (Bahar et al. 2008). Cu ions react with the concrete to form malachite and azurite minerals bound to the concrete surface (Sundberg 1998). Additionally, the alkalinity, and hence pH, of stormwater runoff increases as it contacts concrete (Davis et al. 2010b), which provides environmental benefits by reducing the bioavailable-dissolved form of Cu (Bahar et al. 2008). Even over a distance of 0.61 m on a concrete conduit, ionic Cu was reduced by 7%, 8%, and 13% at a flow rate of 0.75 L/min, 1.5 L/min, and 0.33 L/min, respectively (Perkins et al. 2005). Bahar et al. (2008) found that concretes retention capacity of total Cu varied between 10 - 40% during natural rain events. These studies highlight concretes ability to retain Cu; thus, suggesting that utilising concrete into the pavement design will attenuate Cu, and thus, act as an indirect stormwater treatment. Bahar et al. (2008) and Perkins et al. (2005) found that Cu irreversibly binds to concrete, i.e. little to no desorption of Cu from the concrete occurred, even when the pH of the wash-off decreased. Therefore, concrete can effectively trap Cu resulting in reduced Cu loads in stormwater runoff. In addition, concrete can attenuate dissolved Zn in a process similar to Cu adsorption (Haselbach et al. 2014). Similarly, the stone aggregate in asphalt can have a high capacity for metal adsorption depending on the runoff pH, mineral composition of the aggregate, and the surface area (Lindgren 1996). Thus, asphalt has the potential to retain metal pollutants; however, this is likely to be minimal compared to concrete. Asphalt has the potential to leach organics (e.g. polycyclic aromatic hydrocarbons (PAH's)) from its binder (Sansalone et al. 2008; Sadler et al. 1999), which further deteriorates the quality of the stormwater. In particular, PAH's with 4 rings or less have the highest potential to be leached

from asphalt because of their higher water solubility (Brandt and de Groot 2001). The dominant PAH leached from asphalt is naphthalene, whose concentrations ranged from 1 – 400 ng/l in leaching tests (Brandt and de Groot 2001).

There is a dearth of information regarding how pavement type influences pollutant loads in stormwater; although, pavement composition and roughness can significantly alter the quantity of pollutant loads in stormwater. In particular, very little information is available on the influence of pavement type in retaining atmospherically derived pollutant wash-off, which is a significant component of stormwater pollution sources. This research quantified how much of the key urban pollutants (Cu, Zn, Pb, and TSS) were atmospherically deposited and subsequently washed off from different pavement types (impermeable asphalt, permeable asphalt, impermeable concrete, and permeable concrete) under a variety of natural rainfall events. In addition, the research aimed to identify the best pavement type for attenuating airborne pollutant loads and to identify any pavement type that may be a gross contributor to pollutant loads in stormwater runoff.

#### **4.2. Materials and Methods Overview**

Four different pavement types were used to capture atmospheric pollutant build-up and wash-off at a residential land-use area. The pavement types studied were impermeable asphalt (Asp), impermeable concrete (Con), open-graded porous asphalt (OGPA), and permeable concrete (PCon), as shown in Figure 4-4. Each pavement type had four replicate systems. The Con pavements were constructed using 13 mm aggregate. The matrix was composed of fine aggregate, Portland cement, and water, resulting in a smooth surface. The Asp pavements were constructed using hot mix ‘virgin’ asphalt, comprised of 10 mm maximum aggregate. The PCon pavements were constructed using Portland cement, water, and 6-9 mm aggregate. No fines were included in the mix, so large void spaces were present in the pavements. The OGPA pavements were constructed with hot mix ‘virgin’ asphalt composed of maximum 10 mm aggregate. The mix incorporated some fine aggregate, so the void spaces were smaller

than that of the PCon. After a rain event, stormwater wash-off (separate runoff and infiltrate<sup>6</sup>) was collected and analysed for turbidity, TSS, specific conductivity, pH, alkalinity, dissolved and total Cu, Zn, and Pb. The performance of each pavement type in retaining total Cu, total Zn, and total Pb in BD was conducted using Cohen's *d* effect size (see Section 3.10.1.). Additionally, the stormwater samples were analysed once for PAH's concentrations. PAH's concentrations were determined by RJ Hill Laboratories, an internationally accredited New Zealand laboratory.

In addition, bulk deposition (BD) and wet deposition (WD) samples were collected. WD samples were collected with an N-Con ADS Model 00-120-2 sampler (see Section 3.8.4). The WD sampler opened within 20 seconds of the onset of precipitation and closed within one minute of precipitation concluding. BD samples were collected in a polyethylene container, which was exposed to atmospheric deposition during both dry and wet periods, like the pavements boards. The WD and BD samples were used to determine the quantity of atmospheric metals depositing onto the pavements, and thus, enabling each pavements pollutant retention capabilities to be determined. WD and BD samples were collected 0.45 km away from the experimental board setup for practicality reasons and to avoid public interference with the sampling equipment. Measuring WD and BD at this location was deemed appropriate, as previous research (Chapter 5) found that atmospheric metal deposition did not vary spatially in the Christchurch airside (unless by a hill slope, which was not the case here).

TSS loads from BD were estimated by applying the turbidity concentrations from BD into a TSS-turbidity relationship line. The line ( $R^2 = 0.76$ ) was generated using the turbidity and TSS concentrations from the Con boards as it was assumed that the deposited particulates loads would not be sequestered by the pavement; therefore, representing BD better.

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<sup>6</sup> In this chapter, "wash-off" was used to describe both stormwater runoff from the impermeable surfaces and infiltrate from the permeable surfaces.



**Figure 4-4 The pavement setup in the residential land-use area.**

### **4.3. Results and Discussion**

#### **4.3.1. *Background pollution from the pavement boards***

Prior to deploying the pavements to the field site, initial pollutant background levels from the pavements were monitored. The background water quality from the different pavement boards is exemplified in Table 4-1. Negative values occurred when concentrations of pollutants in the pavement runoff were lower than concentrations of pollutants in the feed water. The negative values represent some form of pollutant retention by the pavement. For all pavement types, the Cu and Pb concentrations were similar to that of the feed water; therefore, Cu and Pb were not leached from any pavement type. For Zn, only PCon and Con had lower concentrations in the effluent, suggesting that utilising concrete in the pavement design will provide better Zn removal. OGPA had similar Zn concentrations to that of the feed water, suggesting that OGPA provided no Zn retention. Therefore, OGPA may not be as efficient at removing Zn as previously suggested by Barrett and Shaw (2007). Conversely, there was an increase in Zn

from the Asp runoff; thus, Asp was leaching Zn from its material. Therefore, any Zn loads obtained from Asp were not representative of just atmospheric deposition, but rather of Zn leaching from the pavement material itself. Therefore, freshly laid Asp has the potential to leach high quantities ( $\approx 344.8 \mu\text{g/l}$ ) of Zn into stormwater runoff. Alkalinity and pH from Con, Asp, and OGPA were similar to the feed water. However, alkalinity and pH increased from PCon, which indicates that minerals (e.g.  $\text{CaCO}_3$ ) were being leached from the pavement material, which could help mitigate metal loads in runoff water (Sansalone et al. 2008). Turbidity levels, a surrogate for suspended solids in this research, were slightly elevated from all pavement types. Therefore, all the pavements were power-washed to remove any residual particles from the pavement structure prior to being deployed in the field. It is likely that residual particles remain on the pavements after construction, which may contribute small, short-term quantities of suspended solid to stormwater.

**Table 4-1 Background pollutant concentrations from the different pavement types (minus the pollutant concentrations from the feed water used by the rainfall simulator). pH of the feed water was 6.7. TSS was below the detection limits.**

Pollutant	Asp	OGPA	Con	PCon
<i>T. Cu (<math>\mu\text{g/l}</math>)</i>	$-3.6 \pm 0.2$	$-2.1 \pm 0.3$	$-2.2 \pm 0.3$	$-3.9 \pm 0.1$
<i>T. Zn (<math>\mu\text{g/l}</math>)</i>	$344.8 \pm 134.6$	$0.4 \pm 5.9$	$-19.3 \pm 0.6$	$-26.8 \pm 0.5$
<i>T. Pb (<math>\mu\text{g/l}</math>)</i>	$-0.2 \pm 0.01$	$-0.1 \pm 0.02$	$-0.1 \pm 0.1$	$-0.2 \pm 0.02$
<i>Turbidity (NTU)</i>	$0.9 \pm 0.2$	$0.89 \pm 0.1$	$0.8 \pm 0.4$	$4.7 \pm 2.3$
<i>Alkalinity (meq/l)</i>	$3.3 \pm 1.5$	$1.9 \pm 0.7$	$-5.0 \pm 1.3$	$345.0 \pm 34.2$
<i>S. Conductivity (<math>\mu\text{S/cm}</math>)</i>	$8.8 \pm 10.3$	$0.2 \pm 0.6$	$-8.9 \pm 2.9$	$1760.7 \pm 181.7$
<i>pH (S.U.)</i>	$7.2 \pm 0.1$	$7.8 \pm 0.1$	$6.9 \pm 0.03$	$12.1 \pm 0.1$

#### 4.3.2. *Summary of rainfall events sampled*

Once the boards were deployed to the study site, surface runoff (from Asp and Con) and infiltrate (from OGPA and PCon) were measured throughout the winter of June 2014 to August 2014. A summary of the rainfall characteristics of each sampling event captured are shown in Table 4-2. For each sampling event, pH, turbidity, and heavy metals were analysed as a minimum. Alkalinity and TSS were only sampled when there was sufficient runoff



volume available for analyses (Table 4-2). The WD and BD samples were sampled for turbidity and heavy metals. However, due to unforeseen construction work occurring next to the deposition samplers, WD and BD was not measured for the final three rain events because the data would have been compromised.

After the main sampling campaign was completed, an additional rainfall event (rain depth (RD) = 7.4 mm, antecedent dry days (ADD) = 12.04 days) was captured 3 months later to determine whether pollutant leaching from the pavements (Asp and OGPA) had changed over time.

**Table 4-2 Rainfall characteristics of each sampling event captured. Where, ADD = antecedent dry days; RD = rain depth; RI = peak hourly rain intensity over the rain event; Dur = rain duration. Where: \* represents TSS not measured and \*\* represents TSS and alkalinity not measured.**

Date	Rain event	ADD (d)	RD (mm)	RI (mm/h)	Dur (h)
13/06/14	1	1.2	17.0	3.6	16
17/06/14	2**	3.5	0.8	0.8	1
18/06/14	3	1.4	5.8	1.8	9
26/06/14	4	7.2	4.2	1.4	6
02/07/14	5*	6.1	2.4	1.2	11
10/07/14	6	6.6	6.2	2	15
17/07/14	7	5.1	10.8	3	19
04/08/14	8*	11.8	2.0	0.8	2
06/08/14	9*	2.7	2.4	1	3
13/08/14	10	3.9	8.0	7.2	2

#### ***4.3.3. Summary of pollutants loads in runoff from different pavement types***

A summary of the stormwater quality from the four different pavement types and from BD and WD is shown in Table 4-3. Boxplots representing the ranges of Cu, Zn, Pb, and TSS loads from each pavement type and BD are exemplified in Figure 4-5. Figure 4-6 illustrates the varying pH and alkalinity from the different pavement types and BD. Table 4-4 illustrates the pollutant removal capabilities of each pavement type.

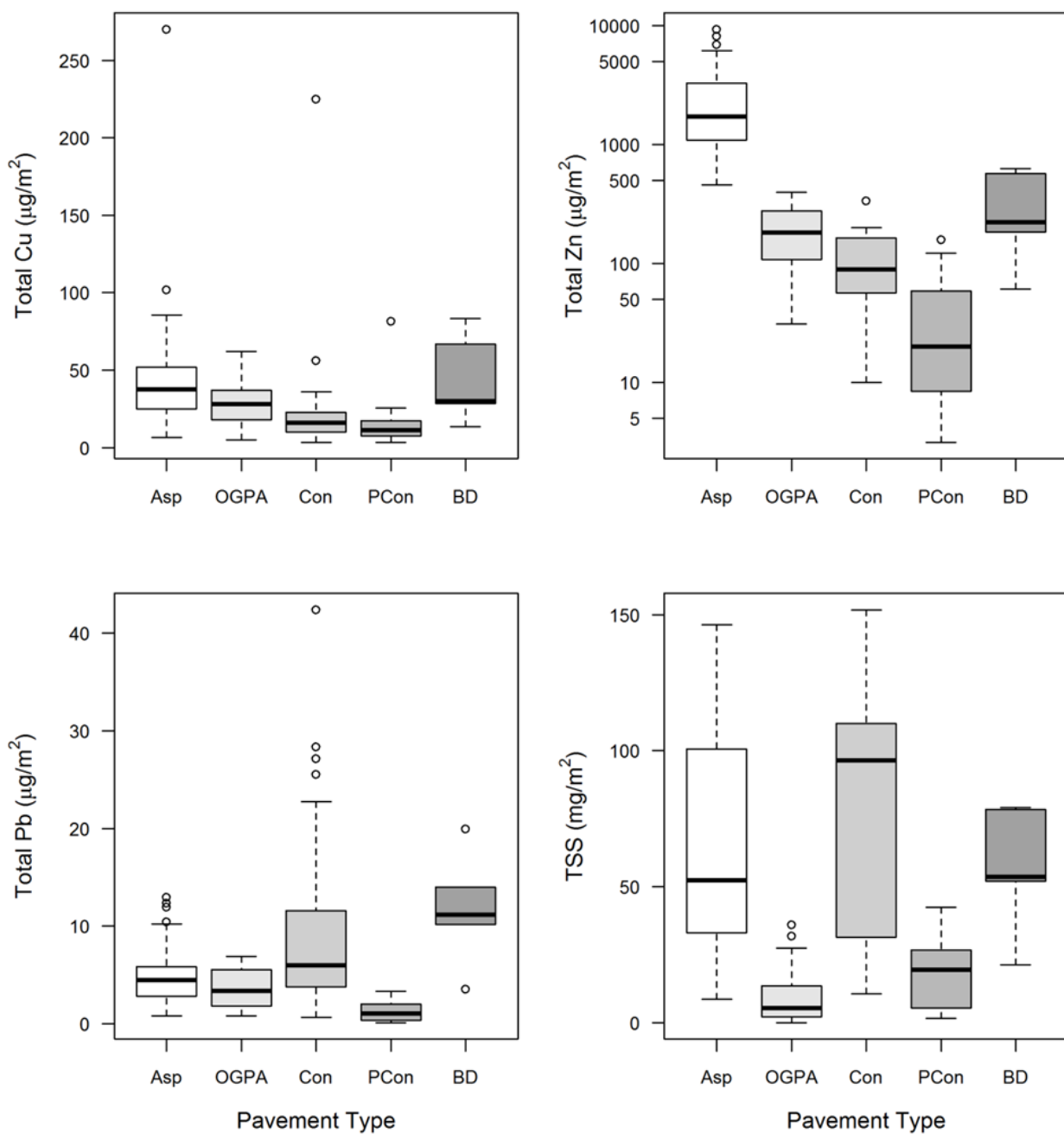
**Table 4-3 Pollutant load ranges from the different pavement types compared to the pollutant loads from bulk deposition (BD) and wet deposition (WD) during a sampling campaign from June 2014 to August 2014.**

<b>Pollutant</b>	<b>Asp</b>	<b>OGPA</b>	<b>Con</b>	<b>PCon</b>	<b>BD</b>	<b>WD</b>
<i>T. Cu</i> ( $\mu\text{g}/\text{m}^2$ )	46.3 $\pm$ 7.3	28.5 $\pm$ 2.2	22.6 $\pm$ 5.5	13.9 $\pm$ 2.0	42.1 $\pm$ 10.0	7.3 $\pm$ 2.3
<i>T. Zn</i> ( $\mu\text{g}/\text{m}^2$ )	2459.4 $\pm$ 372.1	196.5 $\pm$ 15.8	107.4 $\pm$ 10.8	36.5 $\pm$ 6.0	314.3 $\pm$ 85.2	129.6 $\pm$ 52.8*
<i>T. Pb</i> ( $\mu\text{g}/\text{m}^2$ )	5.1 $\pm$ 0.6	3.6 $\pm$ 0.3	9.4 $\pm$ 1.4	1.2 $\pm$ 0.2	11.6 $\pm$ 2.0	5.3 $\pm$ 2.5
<i>D. Cu</i> ( $\mu\text{g}/\text{m}^2$ )	30.3 $\pm$ 3.3	26.1 $\pm$ 2.2	4.8 $\pm$ 0.4	9.7 $\pm$ 1.8	18.3 $\pm$ 5.3	6.6 $\pm$ 2.7
<i>D. Zn</i> ( $\mu\text{g}/\text{m}^2$ )	2332.9 $\pm$ 329.4	186.9 $\pm$ 14.0	39.4 $\pm$ 5.4	7.1 $\pm$ 1.5	223.0 $\pm$ 64.2	109.1 $\pm$ 46.5*
<i>TSS</i> ( $\text{mg}/\text{m}^2$ )	64.8 $\pm$ 8.9	9.8 $\pm$ 2.3	78.4 $\pm$ 10.2	18.1 $\pm$ 2.8	-	-
<i>Turbidity</i> (NTU)	7.1 $\pm$ 1.1	2.5 $\pm$ 0.3	7.6 $\pm$ 1.5	1.7 $\pm$ 0.2	3.5 $\pm$ 1.0	1.0 $\pm$ 0.2
<i>pH</i> (S.U.)	6.4 $\pm$ 0.1	3.6 $\pm$ 0.1	6.4 $\pm$ 0.1	8.9 $\pm$ 0.1	6.0 $\pm$ 0.3	5.5 $\pm$ 0.4
<i>Alkalinity</i> (meq/l )	19.4 $\pm$ 2.2	0	26.5 $\pm$ 1.9	181.6 $\pm$ 15.3	-	-
<i>S. Conductivity</i> ( $\mu\text{S}/\text{cm}$ )	111.7 $\pm$ 7.4	79.1 $\pm$ 7.3	89.0 $\pm$ 5.0	450.9 $\pm$ 35.1	-	-

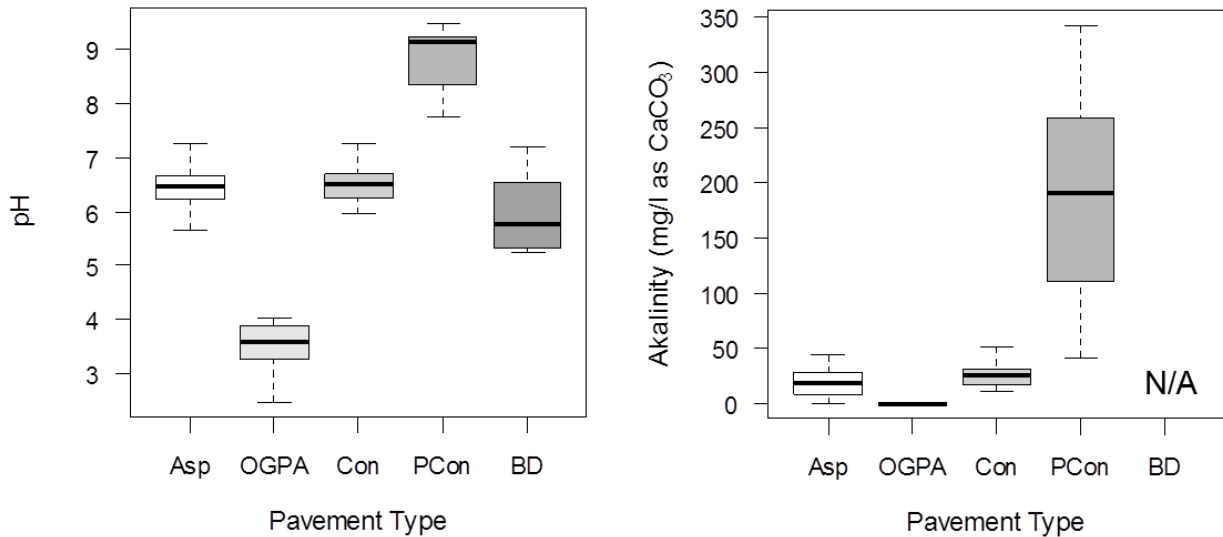
\*WD contributes significant quantities of Zn to BD as discussed in Section 7.3.4.

**Table 4-4 Percentage removal (%) of metal loads from bulk deposition.**

	<b>Asp</b>	<b>Con</b>	<b>OGPA</b>	<b>PCon</b>
<i>T. Cu</i>	-40.5 $\pm$ 38.8	47.8 $\pm$ 5.7	21.1 $\pm$ 16.7	66.7 $\pm$ 9.9
<i>T. Zn</i>	-1895.6 $\pm$ 842.0	47.2 $\pm$ 10.8	9.1 $\pm$ 17.1	83.3 $\pm$ 2.9
<i>T. Pb</i>	54.1 $\pm$ 7.4	16.2 $\pm$ 16.0	60.3 $\pm$ 6.7	84.1 $\pm$ 5.5



**Figure 4-5 A comparison of total Cu, Zn, Pb and TSS loadings in wash-off from different pavement surfaces and from bulk deposition. The box represents the 25<sup>th</sup> (lower) percentile, median, and 75<sup>th</sup> (upper) percentile; the whiskers represent the 5<sup>th</sup> and 95<sup>th</sup> percentiles. Note the varying scales for each pollutant.**



**Figure 4-6 A comparison of pH and alkalinity in wash-off from different pavement surfaces and from bulk deposition. The box represents the 25<sup>th</sup> percentile, median, and 75<sup>th</sup> percentile; the whiskers represent the 5<sup>th</sup> and 95<sup>th</sup> percentiles. Where N/A = not analysed.**

#### 4.3.3.1. Impermeable asphalt (Asp)

Overall, surface runoff from Asp had the highest loads of Cu and Zn compared to the stormwater wash-off from the other pavement types, as exemplified in Table 4-3 and Figure 4-5. This differed to Shaheen (1975), who found no discernable difference in pollutant concentrations between trafficked concrete and asphalt roads in Washington D.C., U.S.A.. Surface runoff from Asp had similar Cu loads to BD (Table 4-3 and Figure 4-5); therefore, Asp provided no retention of Cu, as highlighted by the small effect size ( $d = 0.07$ ). Zn loads from Asp runoff were higher than BD loads (Figure 4-5), which had a large effect size ( $d = 1.54$ ). Moreover, the mean percentage increase of Zn from Asp runoff compared to BD was approximately 1895% (Table 4-4). Therefore, the asphalt material itself was the largest contributor of Zn to runoff. The potential sources of Zn in the Asp were identified as either the aggregate, reclaimed asphalt, or bitumen (although, they had the same bitumen grade). Firstly, as stated by Lindgren (1996), the aggregate can potentially have a high metal content through metal adsorption. However, as the same aggregate source was used in the OGPA mix, it seems unlikely that this was the source of the high Zn levels. Reclaimed asphalt may

contain Zn from previous contact with vehicle tyre wear (Legret et al. 2005). However, only a small quantity of reclaimed asphalt was used in the pavement mix; the majority of the mix was constructed using virgin materials. To definitively rule out the aggregate and reclaimed asphalt as sources of Zn, a leaching test using deionised water was conducted. The test was conducted by mixing 2 g of each material with 100 ml of deionised water for 6 minutes. The resulting leachate was analysed for Zn concentrations. The leaching test intended to mimic Zn leaching from the aggregate and reclaimed asphalt during a high intensity/duration precipitation event. In addition, the aggregate and reclaimed asphalt were digested using the APHA (2005) Method (3030F) to determine how much Zn was trapped within the materials. It was found that for reclaimed asphalt and aggregate only 0.08 mg/kg and 0.05 mg/kg of Zn were leached out, respectively. However, there were much greater quantities of Zn trapped within the materials (61.98 mg/kg of Zn in the reclaimed asphalt and 59.34 mg/kg of Zn in the aggregate). Therefore, the aggregate and reclaimed asphalt were unlikely to contribute greatly to the Zn leaching. Another potential source of Zn may have been from the bitumen. Additionally, because two different bitumens were used for the Asp and OGPA pavements, it would help clarify why Zn leaching only occurred in Asp. This result was unexpected as Kennedy and Gadd (2000) found that in comparison to brake pads and tyre wear, bitumen did not contain any elevated levels of Zn. Although, Kennedy and Gadd (2000) found low values of Zn in raw bitumen (median = 5.5 mg/kg), it was also stated that the Zn content in bitumen will vary from batch to batch depending on the source of the original petroleum product. Thus, the Zn content can vary considerably between asphalt pavements (Horvath and Hendrickson 1998), so it is possible that the bitumen used for the Asp boards had a high water-soluble Zn content. Unfortunately, as the Asp boards were constructed four months prior to testing to enable adequate weathering time to reduce the viscosity of the Asp material (in which the leaching of Zn remained unknown), a sample of the original bitumen used in the Asp mix was not retained for possible material analysis. In addition, it is likely that the Asp was leaching higher quantities of Zn prior to the weathering period; however, this was not quantified. The majority of the Zn loads in the Asp runoff were in the dissolved phase (94.89%), as exemplified in Table 4-5; therefore, increasing the polluting potential of the stormwater runoff.

**Table 4-5 The percentage contribution of dissolved to total Cu and Zn. Note, Pb was not analysed as dissolved Pb was consistently below detection limits.**

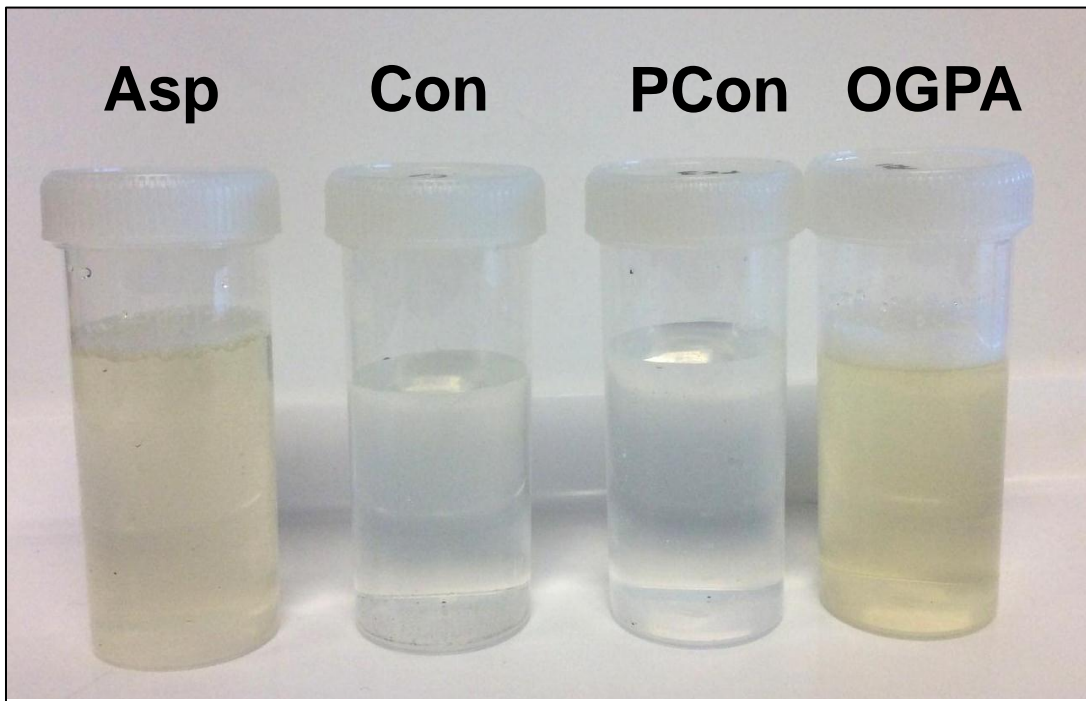
Pavement type	D. Cu / T. Cu (%)	D. Zn / T. Zn (%)
<i>Asp</i>	69.6 ± 2.9	94.9 ± 1.9
<i>OGPA</i>	90.7 ± 1.3	97.0 ± 1.0
<i>Con</i>	32.2 ± 3.1	39.4 ± 3.8
<i>PCon</i>	69.8 ± 2.6	22.1 ± 2.1

As shown in Table 4-3 and Figure 4-5, TSS, turbidity, and Pb loads in runoff from Asp were lower than the loads from BD. Thus, the Asp boards retained TSS and Pb. The Asp boards attenuated TSS and turbidity probably because the deep cavities and the greater adhesion properties of the Asp retained more suspended solids. Similarly, Pb was attenuated (Table 4-4) by the pavement, as Pb was mainly in the particulate phase; therefore, the particulates were entrapped by the pavement surface. This result was similar to Wicke et al. (2012b) who found that asphalt was effective at trapping particulate pollutants in its cavities. Additionally, Vaze et al. (2002) found that a typical storm event, in Melbourne, Australia, did not remove the total particulate load on a pavement, instead, a ‘fixed’ load remained adhered to the surface.

The pH of runoff from Asp was higher than the pH of BD (Table 4-3 and Figure 4-6). This suggests that the physiochemical properties of the Asp boards elevated the pH marginally. The alkalinity of the runoff was slightly lower than the alkalinity from Con. This illustrates (in combination with the background analysis) that the Asp material did not provide any buffering capacity to the runoff. Specific conductivity from Asp remained low (Table 4-3) indicating low mineralisation of the runoff. Minor leaching of naphthalene was observed in runoff from Asp (0.06 µg/l); the concentrations of other PAH’s (e.g. acenaphthene and benzo[a]pyrene) were below the detected limit. Therefore, PAH leaching from Asp was not observed in this research, although, naphthalene leaching was minimal.

Additionally, other water quality parameters that were visually observed, but not measured, were colour and surfactants (Figure 4-7). The runoff from both Asp and OGPA had a yellow/brown colour, which was associated with bitumen leaching from both of the asphalt

pavements. The presence of surfactants in the runoff from both Asp and OGPA likely originated from the addition of anti-stick foam chemicals to the pavement construction equipment (J. Forrest, Fulton Hogan, personal communication, August 18, 2014). The anti-stick foam was used by the asphalt-laying contractors to prevent the hot asphalt mix from sticking to the equipment used to transport the asphalt. It was likely that some of the anti-stick foam was incorporated into the Asp and OGPA material during the transportation phase, and thus, resulted in surfactants leaching into the stormwater.



**Figure 4-7 Image illustrating the reduced surface tension (foam on top of the samples) of runoff from Asp and OGPA, and the difference in runoff colour between the pavement types.**

#### *4.3.3.2. Permeable asphalt (OGPA)*

The Cu and Zn loads in the OGPA infiltrate were relatively similar to that of BD (Figure 4-5) indicating that the OGPA pavement provided no apparent reduction in Cu or Zn loads ( $d =$

0.47 and  $d = 0.10$  for Cu and Zn, respectively). This is further highlighted in Table 4-4, whereby the percentage decrease of Cu and Zn from BD were 21.1% and 9.1%, respectively. The pH of the OGPA infiltrate (average pH 3.6) was lower than the pH from the other pavement types and BD (Figure 4-6). The low pH in the OGPA infiltrate would have facilitated greater Cu and Zn dissolution from the airborne particles deposited on the pavement. This explains why the percentage removal of Cu and Zn was so low - the low pH resulted in the Cu and Zn loads partitioning into the dissolved speciation phase (Pitt et al. 1995), as seen by the high fraction of dissolved to total Cu and Zn in the OGPA infiltrate (90.9% to 97.0% for Cu and Zn, respectively). This explains why the reduction in Cu and Zn loads from OGPA in this study were lower than that reported in other studies. For example, Barret et al. (2007) reported a 75% and 30% reduction in total and dissolved Zn loads, respectively, from OGPA pavements (50 mm thick) compared to conventional asphalt.

Although, the reason for the low pH of the OGPA infiltrate remains unclear, it was possibly from hydrogen sulphide gas being emitted from the asphalt (James and Shahin 1998) resulting in a weak hydrosulphuric acid. Although, the pH was higher in the background pollution test (Table 4-1), this was due to the high alkalinity of the feed water providing some form of buffering which increased the pH. As the precipitate had little/no alkalinity, the pH of the infiltrate remained low.

The OGPA pavement performed better in attenuating Pb loads ( $\approx 60.3\%$  reduction;  $d = 2.00$ ) and TSS loads. TSS loads in the OGPA infiltrate were the lowest from all the pavement types. The efficient removal of TSS and Pb loads was due to the filtering and adhesion capabilities of the OGPA, which entrapped the particulates in the pavements void spaces. Specific conductivity from the OGPA infiltrate remained low (Table 4-3), indicating low mineralisation of the infiltrate. As discussed in Section 4.3.3.1, infiltrate from the OGPA contained colour and surfactants (Figure 4-7). OGPA leached low quantities of naphthalene to runoff ( $0.08 \mu\text{g/l}$ ) - the concentrations of the other PAH's were below the detected limit.



#### 4.3.3.3. Impermeable concrete (Con)

The quantity of airborne Cu, Pb, and Zn loads in runoff from Con were lower compared to the loads in BD (Table 4-3 and Figure 4-5). The Con boards retained more Cu and Zn compared to Asp. This was likely due to the presence of hydroxides in the Con boards adsorbing Cu and Zn. Approximately 47 - 48% of the Cu and Zn loads in BD (Table 4-4) were retained by the Con pavement ( $d = 1.32$  and  $d = 1.22$  for Cu and Zn, respectively). In addition, runoff from Con had lower percentage contributions of dissolved to total Cu and Zn (32.2% and 39.4%, respectively) compared to Asp (62.9% and 94.9%, respectively), as shown in Table 4-5. The pH and alkalinity of Con runoff were similar to that of Asp (Table 4-3 and Figure 4-6), suggesting that the Con pavements had lost their pH buffering capacity since their construction in September 2012. Although most of the alkalinity from Con had been consumed, retention of Zn and Cu still occurred. This is probably due to the high levels of hydroxide species that were still available on the concrete surface. Therefore, metal retention still occurred after the alkalinity had stopped being produced by the concrete pavement. Rushton (2001) also found higher concentrations of Cu, Pb, and Zn (almost double) in runoff from an asphalt surface compared with surfaces paved with either impermeable or permeable concrete.

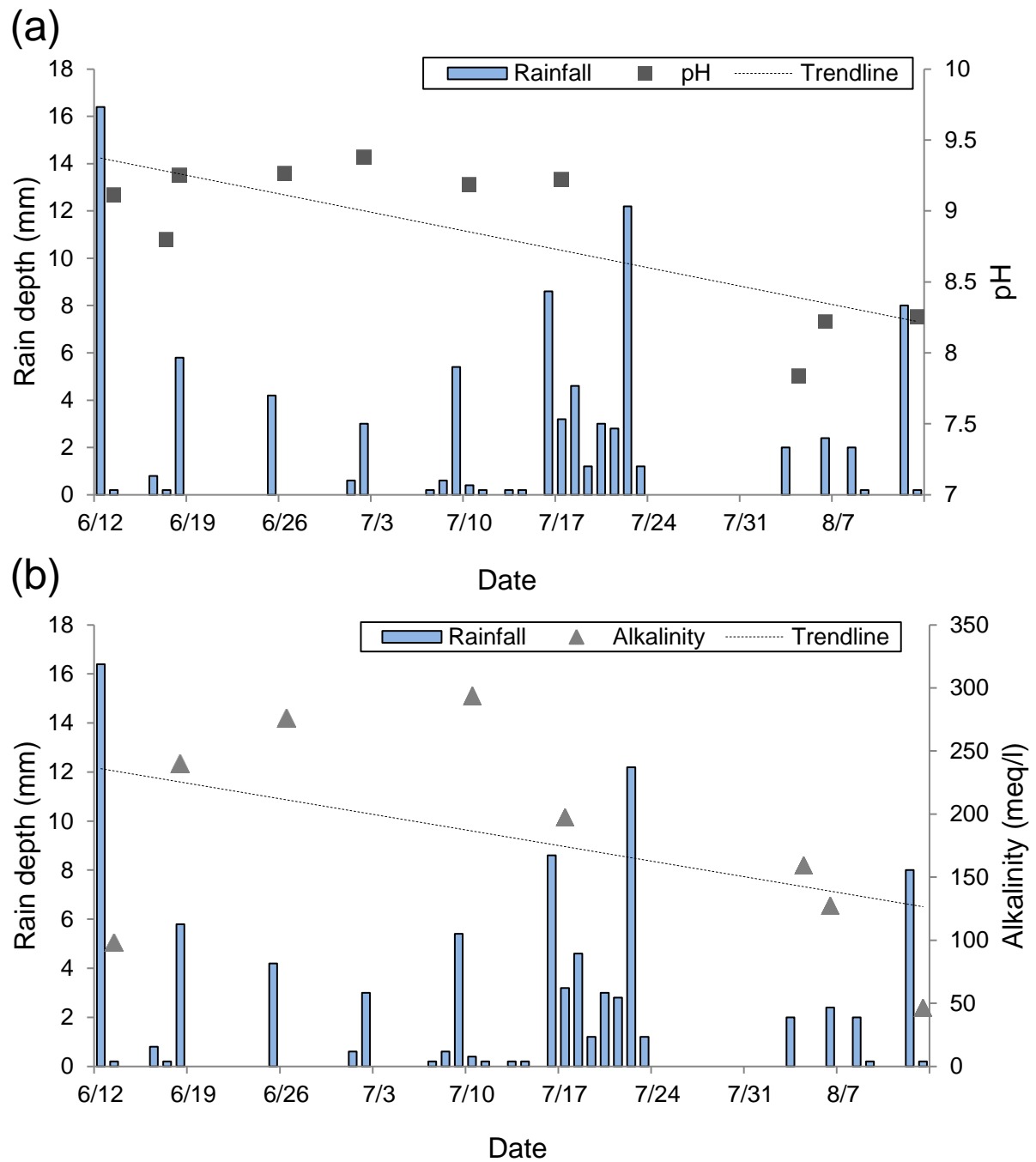
Conversely, the Pb and TSS loads in runoff from the Con boards were the highest of all the pavement types (Figure 4-5). The Con boards only removed 16.0% of the Pb from BD ( $d = 0.44$ ) (Table 4-4). The smoother surface of the Con enabled suspended solids and Pb particulates to be easily dislodged into runoff. The results are similar to Wicke et al. (2012b), who found reduced TSS and Pb loads from a rougher asphalt pavement than a smoother concrete pavement. From the estimated TSS loads in BD, it would appear that the Con pavement itself contributed to TSS loads in runoff, but it is possible that the higher TSS loads was due to the inaccuracies associated with estimating TSS loads in BD from turbidity data. TSS was estimated by applying the TSS-turbidity relationship derived for Con to the BD turbidity data. This lead to inaccuracies in estimating TSS loads in BD, as it had to be assumed that Con did not retain any particulates, which was an invalid assumption. To improve the Pb and TSS attenuation of Con, its surface roughness should be increased by

surface texturing techniques to enable more trapping of particulates within the cavities and enhance skid resistance. Specific conductivity from Con remained low (Table 4-3), indicating low mineralisation of the runoff. No leaching of PAH's from Con was observed.

#### 4.3.3.4. *Permeable concrete (PCon)*

The PCon pavement, like Con, reduced Zn and Cu loads compared with BD ( $d = 1.66$  and  $d = 2.22$  for Cu and Zn, respectively) due to the Zn and Cu retention capabilities of the concrete (Haselbach et al. 2014). PCon provided a greater reduction in Cu and Zn loads than that of Con, due to the increased contact time and the increased surface area for pollutant-concrete interactions as the stormwater passed through the flow channels of the PCon. Similarly, Bahar et al. (2008) found that the amount of Cu retained by concrete was related to the exposed concrete surface area and the contact time. Increasing the surface area resulted in a greater number of sites that were available for surface adsorption from either complexation or solid formation with the hydroxides and carbonates in the concrete (Haselbach et al. 2014). Moreover, the reduction of Cu and Zn could also be associated with increased solid retention by the pavers' voids (Legret et al. 1996). The PCon pavement provided the best removal of dissolved Zn (Table 4-3) and had the lowest proportion of dissolved Zn to total Zn (Table 4-5). Similarly, Dierkes et al. (1999) found that permeable concrete was highly effective at trapping dissolved heavy metals in runoff. The pH of the PCon infiltrate was higher due to the carbonate alkalinity of the infiltrate (Aziz et al. 2001), which was responsible for some heavy metal retention through complexation (Haselbach et al. 2014). However, the pH and alkalinity from the PCon were reducing over the sampling campaign (Figure 4-8). Therefore, like the Con, the PCon pavement would eventually stop producing alkalinity as the pavements are exposed to more sunlight, wind, and rainfall. However, like Con, it is assumed that the PCon pavement would continue to retain metals even when the pH and alkalinity has stabilised. This is due to the high levels of hydroxide species available in the PCon for Cu and Zn to react (Haselbach et al. 2014). Specific conductivity from the PCon infiltrate was high (Table 4-3), indicating mineralisation of the infiltrate by  $\text{CaCO}_3$ . No leaching of PAH's from PCon was observed.

Similarly to the OGPA pavement, the PCon infiltrate had lower Pb and TSS loads compared to BD and runoff from the impermeable pavements due to the permeable system filtering out particulate pollutants. The OGPA provided greater TSS removal than PCon due to the smaller void spaces in the OGPA, which filtered out more particulates. It is assumed that the PCon pavement would perform similarly to OGPA if the PCon paver incorporated more fine aggregate into its mix (hence reducing the size of the void spaces). However, the PCon reformed better than OGPA at removing Pb, which was associated with the PCon adsorbing some quantity of Pb in a process similar to Cu and Zn.



**Figure 4-8 Changes to (a) pH and (b) alkalinity from PCon throughout the sampling campaign.**

#### 4.3.4. *Ecotoxicity of stormwater*

Average concentrations ( $\mu\text{g/l}$ ) of dissolved Cu and Zn (dissolved Pb was not analysed as it was frequently below detection limits ( $1 \mu\text{g/l}$ )) were compared with the relevant effects-based ecotoxicological thresholds for safeguarding 90% of freshwater species (ANZECC 2000) to assess the potential ecotoxicity (Table 4-6). The ecotoxicological thresholds had to be adjusted for hardness because as hardness increases, ecotoxicity decreases. As the alkalinity concentrations (used as a representative for hardness) were only high for PCon, the ecotoxicological thresholds were modified for PCon only using the following equations (ANZECC 2000):

$$\text{Cu HMTV} = \text{TV}(\text{H}/30)^{0.85} \quad \text{eq. 4-1}$$

$$\text{Zn HMTV} = \text{TV}(\text{H}/30)^{0.85} \quad \text{eq. 4-2}$$

Where: HMTV = hardness-modified trigger value ( $\mu\text{g/l}$ ); TV = trigger values ( $\mu\text{g/l}$ ) at a hardness of  $30 \text{ mg/l}$  as  $\text{CaCO}_3$ ; H = measured hardness ( $\text{mg/l}$  as  $\text{CaCO}_3$ ) of a fresh surface water ( $\leq 2.5\%$ ).

Alkalinity was used to represent hardness concentrations from PCon as it was assumed that the alkalinity was only associated with  $\text{CaCO}_3$ , and thus, be equivalent to hardness (Wilson 2010). Dissolved Cu and Zn ecotoxicological thresholds were exceeded by Asp and OGPA. Indicating that at least 10% of aquatic species would be adversely effected by wash-off from Asp and OGPA if it were directed to an urban waterway untreated. However, these concentrations would be diluted once entered into the waterway, and thus, reducing its ecotoxicity potential. Dissolved Cu and Zn ecotoxicological thresholds were not exceeded by Con and PCon; therefore, runoff from these pavement types will not be harmful to 90% of aquatic species.

**Table 4-6 Average concentrations ( $\mu\text{g/l}$ ) of Cu and Zn in wash-off from each pavement type compared with the 90% ANZECC ecotoxicological guidelines and the hardness-dependent 90% ANZECC ecotoxicological guidelines for PCon only.**

	ANZECC 90%	Asp	OGPA	Con	ANZECC 90% modified	PCon
<i>d.Zn</i>	15.0	$313.1 \pm 38.9$	$52.0 \pm 4.5$	$7.5 \pm 1.1$	69.3	$1.3 \pm 0.2$
<i>d.Cu</i>	1.8	$4.4 \pm 0.5$	$8.1 \pm 1.3$	$1.2 \pm 0.2$	8.3	$3.3 \pm 0.9$

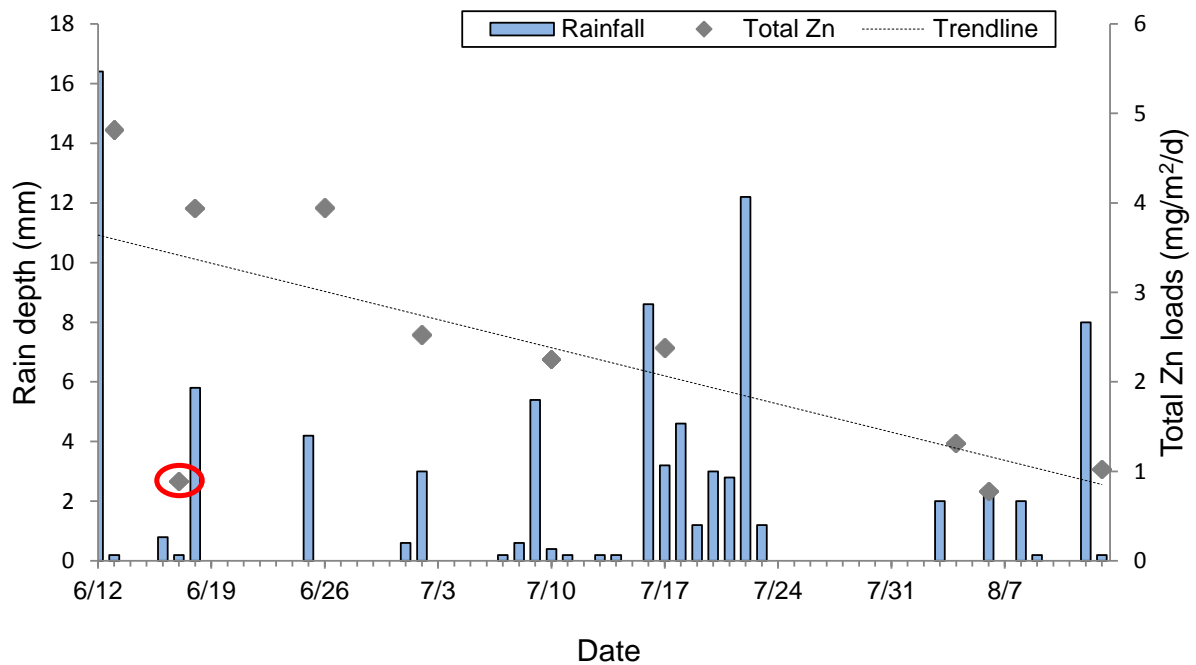
#### **4.3.5. Behaviour of pavement leaching over time**

Both asphalt pavement types, OGPA and Asp, showed increased Zn loads and reduced pH compared to concrete. However, the leaching of pollutants from OGPA and Asp appeared to be diminishing over time, as exemplified in Figure 4-9 and Figure 4-10. During the sampling campaign, a decrease in total Zn load per antecedent dry day was observed and it was assumed that the Zn leaching would continue to decrease over time until the Asp reached maturation from weathering. Because the Asp boards were exposed to the elements for four months prior to sampling, it was likely that the Asp was leaching higher Zn loads immediately after construction and this had been diminishing over time. The pH of the infiltrate from OGPA was increasing over time as the hydrosulphuric acid leaching decreased. Therefore, it is assumed that, with time, the infiltrate from the OGPA would have a pH similar to that of the other pavements. This could potentially increase the retention capacity of Cu and Zn as metals tend to partition into the particulate phase with increased pH; therefore, more metal particulates would be filtered out as the stormwater passed through the flow channels of the OGPA.

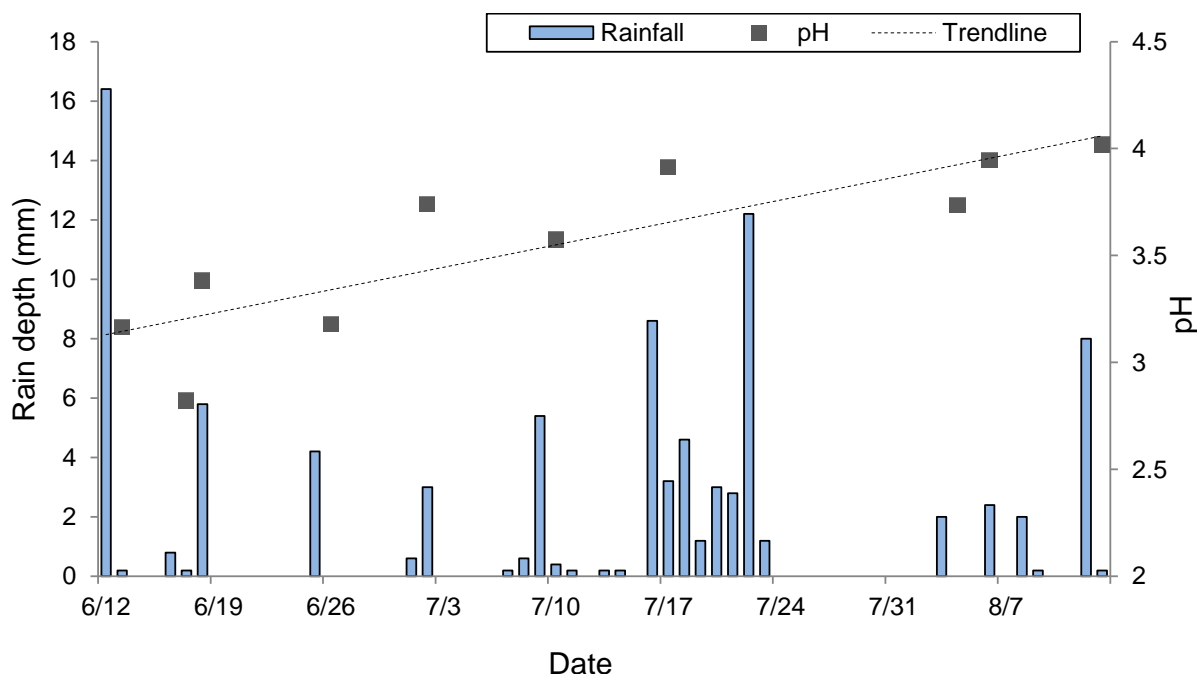
Three months after the sampling campaign was completed an additional rain event was sampled to evaluate how pollutant leaching from the OGPA and Asp behaved over time. The pH of the OGPA infiltrate from this latest sampling event was low ( $\text{pH} = 3.1$ ). It is assumed that the pH of the infiltrate was lower than previous rain events captured because of the longer antecedent dry period (12 days). Therefore, after 6 months of weathering the OGPA infiltrate still had a low pH. The Zn load of the Asp runoff was lower ( $0.12 \text{ mg/m}^2/\text{d}$ ) than Zn loads

obtained during the sampling campaign; therefore, runoff from the Asp continued to show a diminishing trend of Zn leaching.

However, when vehicular activity is applied to a pavement, the pavement will be worn away (Luhana et al. 2004). This is particularly the case when studded tyres are used in colder countries (Lindgren 1996). As the pavement is being worn away by abrasion, it may never reach maturation. Instead, the abrasion forces will reveal a fresh surface layer that can readily leach Zn to the wash-off, or decrease the wash-off pH. Determining the how the maturation process is effected by vehicle abrasion is beyond the scope of this paper, but it is recommended that further research be conducted into this topic.



**Figure 4-9 Changes to Zn loads per antecedent dry day from the asphalt pavement (Asp) throughout the sampling campaign. The low Zn load on sampling event two (circled) was associated with the low rainfall that occurred for that sampling event (0.8 mm).**



**Figure 4-10 Changes to pH from the permeable asphalt pavements (OGPA) throughout the sampling campaign.**

#### **4.4. Pavement-pollution interactions from a trafficked road**

This paper solely focused on how pavement composition and roughness influenced atmospherically derived pollutant wash-off. However, in a real world situation, pollutant wash-off will differ when traffic is applied to the pavement. Firstly, the source of pollutants on a pavement will not be limited to atmospheric deposition. Additional sources of pollutants include tyre wear, brake lining wear, exhaust fumes, road construction, resuspension of road dust, car catalysts, and road paint abrasion (Adachi and Tainosho 2004; Sternbeck et al. 2002; Beasley and Kneale 2002). Therefore, pollutant loads in wash-off from trafficked pavements will be greater than from non-trafficked pavements. In addition, particulate pollutants on trafficked pavements typically have a coarser size fraction than particles derived from atmospheric deposition. For example, Zhao et al. (2010) found that 60% - 75% of particles in wash-off from a road were less than 250  $\mu\text{m}$ , of which, particles between 62  $\mu\text{m}$  – 105  $\mu\text{m}$  were the most abundant. Approximately 70% of atmospherically deposited pollutants are below the 30  $\mu\text{m}$  size range (Cao et al. 2011). Because smaller particles are more easily



washed-off than larger particles (Egodawatta et al. 2007), atmospherically derived pollutants are more likely to be dislodged during a rain event. Finally, the effect of traffic-induced resuspension was not taken into account in this research. Traffic induced resuspension occurs due to tyre-surface interactions and vehicle induced turbulence on pavements (Berger and Denby 2011). Traffic-induced resuspension on a pavement is an important pollutant removal process (Luhana et al. 2004) and source of atmospheric particulate matter (Rogge et al. 1993; Ruellan and Cachier 2001). According to Lenschow et al. (2001) 50% of the ambient concentrations of PM<sub>10</sub> near a busy street in Berlin were due to traffic-induced resuspension. Resuspension rates are effected by the car type, vehicle speed, particle size, traffic numbers, pavement roughness, and the surface moisture content on the pavement (Nicholson and Branson 1990; Sehmel 1973). For example, pollutant resuspension will occur more easily on a smooth surface than on a rougher, irregular surface, which traps more particles (Sehmel 1973). Monitoring the effect of pavement composition and roughness on atmospherically derived pollutant wash-off on a trafficked road is inherently complex and beyond the scope of this paper. Instead, this paper represents a simplified pavement system, whereby, atmospheric deposition is the only pollutant source and vehicle-induced resuspension forces are not applied. Therefore, the results on pollutant wash-off loads should be used with caution – pollutant wash-off from pavements may be different under trafficked conditions. However, the concepts of pollutant retention, as discussed here, will remain the same whether traffic is applied to a pavement or not; concrete will adsorb Cu and Zn and a rougher surface will entrap more pollutants.

#### **4.5. Conclusion**

To minimise the burden of atmospheric deposition as a source of stormwater pollution, more emphasis needs to be placed on the influence of pavement type in attenuating airborne (and other) pollutant wash-off. PPS are effective at removing TSS; however, the type of pavement used in the PPS will affect total heavy metal load reductions. In particular, incorporating PCon into a PPS will provide much better immobilisation of dissolved and total heavy metals loads in stormwater runoff. However, in some instances, PPS are not always suitable for use,

e.g. on a high gradient terrain, and impermeable pavements are more appropriate. Utilising Con instead of the more commonly used Asp will provide better heavy metal reduction; although, TSS will be higher from the smoother Con. However, this could be minimised by increasing the surface roughness of the Con by surface texturing techniques. Alternatively, a sediment filter should be used in conjunction with the Con pavement for TSS reduction. Where a permeable pavement layer is required on top of an impermeable pavement for increased road safety, it is recommended that PCon be utilised instead of the more commonly used OGPA because it will provide better metal pollutant retention. With time, the PCon will stop producing alkalinity (like Con) and the pollutant retention capabilities of PCon will be reduced. However, the PCon will still provide greater pollutant retention than its asphalt counterpart due to the hydroxides in the PCon still providing adsorption sites for Cu and Zn ions. Results from this research suggested that asphalt may not be as inert as originally thought – it can leach high quantities of Zn and can decrease the pH of stormwater. Although, the Zn leaching was reducing over time as the Asp matured. It is recommended that a more detailed analysis on Asp and bitumen be conducted for a better understanding of Asp's polluting potential.

# Chapter Five: Atmospherically Derived Pollutants in Stormwater Runoff from Different Land-Use Areas

## 5. ATMOSPHERICALLY DERIVED POLLUTANTS IN STORMWATER RUNOFF FROM DIFFERENT LAND-USE AREAS

### 5.1. Introduction

Heavy metals in the atmosphere are associated with atmospheric particles (Morselli et al. 1999). These particles are transported from the atmosphere to the ground by either dry deposition or wet deposition (as discussed in Section 2.2). Atmospheric deposition can be a substantial source of metals to waterways (Sabin et al. 2005). However, the amount of atmospheric metal deposition will be dependent on land-use activities and on atmospheric deposition rates (principally dry deposition). Dry deposition is driven by the atmospheric concentration of the depositing species, the species chemical and physical properties', atmospheric motion (i.e. turbulence and wind), and the capability of the surface to entrap the depositing species (Davidson and Wu 1990; Erisman and Draaijers 2003). In particular, wind speed and particle size are the dominant controls for dry deposition (Noll et al. 1988). Higher wind speeds and turbulence increases the efficiency of the particle to be transported to the receptors surface (Erisman and Draaijers 2003). The effects of wind speed and turbulence on dry deposition velocities,  $v_d$ , have been previously described by the following equation (Seinfeld and Pandis 2006):

$$v_d = \frac{1}{r_a + r_b + r_a r_b v_s} + v_s \quad \text{eq. 5-1}$$

Where  $r_a$  is the aerodynamic resistance connected with the turbulent transfer of pollutants across the boundary layer;  $r_b$  is the quasi-laminar resistance associated with the transfer of pollutants across the near surface layer;  $v_s$  is the particle settling velocity. Atmospheric motion, namely wind speed and turbulence, affect  $r_a$  and  $r_b$  in air; generally, there is a decrease in  $r_a + r_b$  when wind speed increases (Seinfeld and Pandis 2006). Therefore, the atmospheric deposition rate (or dry deposition velocities,  $v_d$ ) increases when wind speed, and thus turbulence, increases. Topography is another important factor affecting dry deposition as it influences many aerodynamic parameters (e.g. air velocity, wind direction, and turbulence)

(Goossens 1988). At the start of a windward slope (on a hillside), the deposition rate begins to increase from the baseline (flat terrain) conditions due to an increase in wind speed. Deposition then reaches a maximum at the point where the slope changes from concave to convex (inflection line) before decreasing as the atmospheric turbulence intensity decreases over the convex surface (Goossens 1988, 1996). Deposition is significantly reduced from the baseline condition all over the leeward face of a slope as the air flow (and subsequently dust) blows over the hill; thus avoiding the leeward slope (Goossens 1988, 1996). Parker and Kinnersley (2004) found deposition increased by a factor of 0.9 – 1.7 when on the windward side of a slope in comparison to its flat counterpart. In addition, pollutant properties (e.g. particle density, particle diameter) control the pollutant's affinity to be transported through the atmosphere via Brownian diffusion, eddy diffusion, and gravity settling (Sehmel 1980a). Surface properties influence a particle's ability to be entrapped by the surface (as detailed in Sehmel (1980a)).

Atmospheric deposition of metals is dependent on atmospheric metal concentrations, which vary locally and regionally due to different quantities of emission sources. For example, variations in heavy metals concentrations within the European Union was observed by Lavín et al. (2001), which found that Eastern Europe, because of the greater source emissions of heavy metals to the atmosphere, had higher atmospheric heavy metal concentration than Western Europe. Even within the same regional area, atmospheric metal concentrations are highly variable. Paode et al. (1998) found higher concentrations of Cu, Zn, and Pb deposited in an urban area in Illinois, U.S. compared to a near-urban and a rural area; furthermore, the near-urban area had higher deposition fluxes than the rural area for Cu and Zn only. Sabin et al. (2006) found that atmospheric Pb concentrations were uniform in different urban sites in L.A., U.S.A.; however, there were significantly lower concentrations of Cu and Zn in one particular area due to lower source emissions and its location upwind from major source emissions. Similarly, Gunawardena et al. (2011) found higher particulate deposition loads in an urban land-use area than a suburban land-use area, which was associated with greater anthropogenic and traffic activities occurring in the urban area. Lim et al. (2006) found that dry deposition fluxes were similar for urban areas in Los Angeles Region, U.S., but deposition fluxes were lower at a non-urban site. González-Miqueo et al. (2009) reported

spatial heterogeneous distributions of atmospheric heavy metal deposition in Navarra, Spain, due to different localised emission sources. Furthermore, even within the same urban area, pollutant deposition can be highly variable. For example, Lynam et al. (2014) found considerable variations in trace metal loads in wet deposition between 8 different sites in central Illinois, U.S.A..

Despite these studies, there remains a dearth of knowledge regarding the significance of land-use area on atmospheric deposition in urban stormwater pollution. The objective of this research was thus to identify how different land-use activity (industrial, residential, and airside) influenced atmospherically derived pollutants in stormwater runoff. Industrial and residential areas were chosen because previous international research indicated that industrial activity would produce higher stormwater pollutant loads than residential activity (Sartor et al. 1974). Airside was chosen as a study site because the influence of airport activities on atmospherically derived pollutants in stormwater runoff had not been previously investigated. Christchurch airport is a prominent land-use near the city, and airport activities in general are considered to be a significant source of pollutants to the environment (Onasch et al. 2009). For example, Fang et al. (2007a) found 0.5 – 0.7 times higher particulate matter concentrations at an airport than a suburban site in Taiwan. The methodology employed in this research enabled the long-term trends of atmospheric deposition in stormwater to be examined in the different land-use areas simultaneously over a long period (approximately one year), covering a wide range of meteorological regimes.

## **5.2. Materials and Methods Overview**

Modular concrete boards were deployed in a residential, industrial, and airside land-use areas in Christchurch, New Zealand. Four replicate boards ( $\approx 1 \text{ m}^2$ ), elevated  $\approx 0.5 \text{ m}$  above ground at a  $4^\circ$  slope, were placed in each land-use area. Runoff from the boards was collected and analysed for TSS, Cu, Pb, and Zn after different rain events. Other chemical parameters (pH, alkalinity, conductivity, and turbidity) were also analysed. Results were analysed using

different statistical techniques, such as, principal component analysis (PCA) and multivariate analysis of variance (MANOVA).

### **5.3. Results and Discussion**

#### ***5.3.1. Background pollution from the impermeable concrete boards***

Background pollution from the impermeable concrete boards are exemplified in Table 5-1. Discussion on how the background analysis was conducted can be found in Section 4.3.1. Negative values occurred when the concentrations of pollutants in the pavement runoff were lower than the concentrations of pollutants in the feed water. The negative values represent some form of pollutant retention by the concrete. The impermeable concrete boards did not leach any heavy metals from its material. All the boards provided good Zn retention due to the carbonates and hydroxides in the concrete adsorbing Zn. The pH, alkalinity, and conductivity were high for all the boards; therefore,  $\text{CaCO}_3$  ions were being leached from the concrete. The turbidity and TSS concentrations from all the boards were elevated due to residual particles from the construction stage being washed-off. Therefore, the boards were power-washed to remove any remaining particles. In addition, the boards were deployed to the field for two months prior to testing so the boards could stabilise (i.e.  $\text{CaCO}_3$  leaching was minimal).

**Table 5-1 Background pollutant concentrations (mean  $\pm$  SE) from the impermeable concrete boards from each land-use area studied (minus the pollutant concentrations from the feed water used by the rainfall simulator). pH of the feed water was 6.19.**

<b>Pollutant</b>	<b>Airside</b>	<b>Residential</b>	<b>Industrial</b>
<i>Total Cu (<math>\mu\text{g/l}</math>)</i>	$-2.6 \pm 0.1$	$0.6 \pm 1.2$	$-2.5 \pm 0.1$
<i>Total Zn (<math>\mu\text{g/l}</math>)</i>	$-48.3 \pm 0.7$	$-47.6 \pm 1.2$	$-48.8 \pm 0.6$
<i>Total Pb (<math>\mu\text{g/l}</math>)</i>	$0.02 \pm 0.05$	$0.04 \pm 0.02$	$-0.06 \pm 0.01$
<i>TSS (mg/l)</i>	$27.2 \pm 9.3$	$6.1 \pm 1.5$	$7.31 \pm 3.3$
<i>Turbidity (NTU)</i>	$25.4 \pm 7.8$	$10.4 \pm 4.9$	$22.6 \pm 7.4$
<i>Conductivity (<math>\mu\text{S/cm}</math>)</i>	$675.3 \pm 127.8$	$394.6 \pm 66.8$	$783.5 \pm 303.1$
<i>Alkalinity (meq/l)</i>	$133.1 \pm 29.2$	$75.3 \pm 18.7$	$160.9 \pm 67.4$
<i>pH (S.U.)</i>	$11.5 \pm 0.1$	$10.9 \pm 0.2$	$11.2 \pm 0.2$

### 5.3.2. Summary of rain events captured

Twenty-four separate rain events (events that occurred in each land-use area) were collected from February to December 2013; Table 5-2 details the number of events collected within different rainfall parameter ranges (antecedent dry days, rain depth, and peak rain intensity).

**Table 5-2 Number of rain events captured that conformed to different meteorological criteria.**

	<b>ADD (d)</b>			<b>RD (mm)</b>			<b>RI (mm/h)</b>		
	<b><math>\leq 2</math></b>	<b>3-6</b>	<b><math>&gt; 6</math></b>	<b><math>\leq 5</math></b>	<b>5-15</b>	<b><math>&gt; 15</math></b>	<b><math>\leq 1</math></b>	<b>1.1-3</b>	<b><math>&gt; 3</math></b>
<i>Ind</i>	7	7	10	9	9	6	10	9	5
<i>Res</i>	7	7	10	8	7	9	5	11	8
<i>Air</i>	7	6	11	10	10	4	8	10	6

### 5.3.3. Summary of pollutants loads in runoff

A summary of the pollutant loads are represented in Table 5-3. Specific conductivity of the runoff from each land-use area was low indicating low mineralisation of the runoff. The pH and alkalinity of the runoff from each land-use area were similar. In addition, the values for alkalinity were low; therefore, most of the alkalinity from all the concrete boards had been



consumed. Discussion on heavy metal and TSS variations between the different land-use areas are in the following sections.

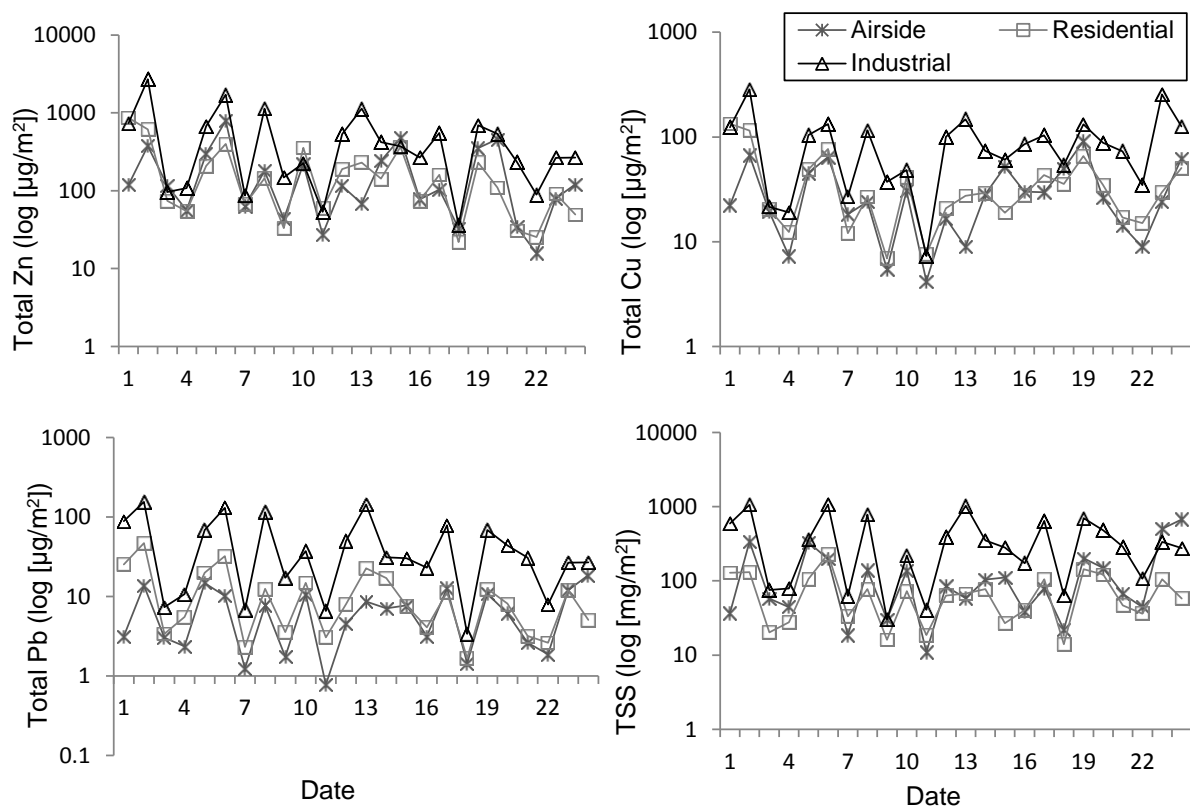
**Table 5-3 Pollutant load ranges from the impermeable concrete boards for each land-use area studied. Note dissolved Pb was not analysed as it was frequently below the detection limit.**

<b>Pollutant</b>	<b>Airside</b>	<b>Residential</b>	<b>Industrial</b>
<i>Total Cu (<math>\mu\text{g}/\text{m}^2</math>)</i>	$30.3 \pm 2.8$	$36.8 \pm 3.2$	$87.8 \pm 6.8$
<i>Dissolved Cu (<math>\mu\text{g}/\text{m}^2</math>)</i>	$12.1 \pm 1.2$	$17.4 \pm 2.2$	$29.7 \pm 4.2$
<i>Total Zn (<math>\mu\text{g}/\text{m}^2</math>)</i>	$180.3 \pm 24.1$	$176.7 \pm 20.6$	$505.2 \pm 63.0$
<i>Dissolved Zn (<math>\mu\text{g}/\text{m}^2</math>)</i>	$70.9 \pm 7.8$	$86.9 \pm 11.9$	$141.9 \pm 4.2$
<i>Total Pb (<math>\mu\text{g}/\text{m}^2</math>)</i>	$6.7 \pm 0.6$	$11.4 \pm 1.2$	$46.8 \pm 4.7$
<i>TSS (<math>\text{mg}/\text{m}^2</math>)</i>	$139.5 \pm 17.8$	$68.5 \pm 5.3$	$364.3 \pm 33.6$
<i>Turbidity (NTU)</i>	$7.2 \pm 0.7$	$4.5 \pm 0.4$	$15.6 \pm 1.3$
<i>S. Conductivity (<math>\mu\text{S}/\text{cm}</math>)</i>	$68.6 \pm 2.5$	$71.4 \pm 3.7$	$84.7 \pm 4.1$
<i>Alkalinity (<math>\text{meq}/\text{l}</math>)</i>	$39.5 \pm 5.6$	$33.2 \pm 4.0$	$34.1 \pm 3.7$
<i>pH (S.U.)</i>	$7.2 \pm 0.1$	$7.1 \pm 0.04$	$7.0 \pm 0.1$

#### **5.3.4. Spatial pattern of atmospherically derived pollutants in stormwater runoff**

The variance between total Cu, Pb, Zn and TSS within each land-use area could be explained by one principal component, suggesting that within each land-use area the pollutant loads originated from a single source. The mean loads of total Cu, Zn, Pb and TSS differed significantly *between* the land-use areas (Pillai's trace [ $V = 0.878$ ,  $F(8, 134) = 13.113$ ,  $p > 0.001$ ]). The Ind area was significantly different from the Res and Air areas. However, Res and Air had statistically similar mean pollutant loads to each other except for TSS. All land-use areas exhibited similar trends for metal and TSS loads (Figure 5-1), exemplified by similar patterns of increasing and decreasing pollutant loads over time, with Ind consistently higher than the other land-use areas. The similar temporal trends suggest that atmospherically deposited pollutants had a homogenous distribution within the wider Christchurch airshed. Wilson et al. (2006), however, conducted a study into wintertime  $\text{PM}_{10}$  concentrations in Christchurch and found conflicting data with no uniform distributions at an intra-urban

(within city) scale. Furthermore, Kossman and Sturman (2004) found higher wintertime concentrations of carbon monoxide (CO) and PM<sub>10</sub> in the residential area of Coles Place (approximately 3.8 km from the Res research site), compared to the industrial area of Woolston (approximately 1.4 km from the industrial research site). The lower concentrations of PM<sub>10</sub> and CO in the industrial area were associated with the cold air drainage (katabatic wind) from an adjacent hill range (Port Hills) that conveyed relatively clean air inland from the coast. These studies, however, measured snapshots of fine pollutant particles in the atmosphere and not of particles being deposited on surfaces between rainfall events. The homogenous distribution of metal and TSS loads within the Christchurch airshed (found in this study) may be due to these pollutants being associated with different particles size ranges.



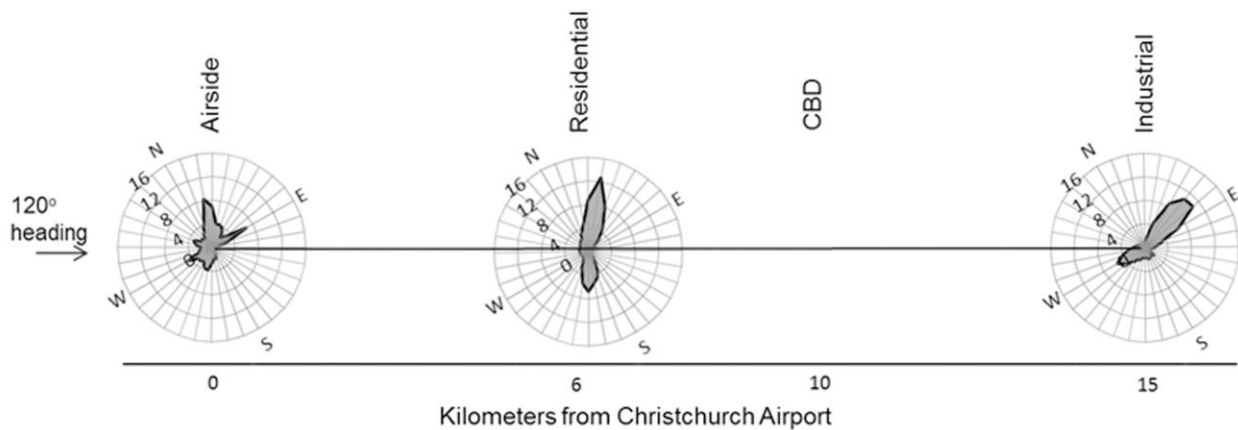
**Figure 5-1 Airborne pollutant loads in stormwater runoff from 24 different dates when rainfall occurred in all three receptor sites - the rainfall characteristics of each date will slightly differ between land-use areas due to localised rainfall patterns within each the catchment**

Atmospheric pollutant ratios (as used by Rahn (1981)) were generated for all land-use sites throughout the monitoring period to ascertain if pollutants likely originated from the same atmospheric source (Table 5-4). Cu was used as the common divider between each metal studied because its mean load was midway between the highest (Zn) and lowest (Sb) mean pollutant loads. The mean ratios of Zn to Cu (4.9 – 5.6) were statistically similar between all three land-use areas, along with As/Cu (0.2) and Sb/Cu (0.03). Res and Air had a statistically similar mean for Pb. Conversely, Cr and Mn to Cu ratios were statistically different between Res and Air, but similar between Air and Ind. Ni was the only element studied for which Res and Ind was statistically similar, but this did not hold for Air. The ratios (Zn, Pb, As, and Sb) were relatively homogeneous between the three land-use areas. This suggests that the pollutants originate from a similar source(s). Furthermore, it can be deduced that land-use area was not a primary factor for influencing pollutant loads in stormwater runoff because the trends and the elemental ratios to Cu were similar between the three research sites. In addition, pollutants originating from one land-use area were unlikely to be transported downwind to the other sites except during an extreme northwest wind, which do not frequently occur (Figure 5-2).

Wicke et al. (2012b) conducted a preceding study on atmospheric pollutant contribution to stormwater runoff in a carpark near the Res testing site. They found similar airborne metal ratios in two locations of the carpark (Zn to Cu =  $6.3_{(\text{mean})} \pm 0.5_{(\text{SE})}$ ; Pb to Cu =  $0.4_{(\text{mean})} \pm 0.01_{(\text{SE})}$ ). The experiments of Wicke et al. (2012b) were conducted in 2009/2010 prior to the 2011 major Christchurch earthquakes, which resulted in most of the central business district (CBD) being demolished. The demolition of the CBD resulted in significant quantities of particulate matter being released in the Christchurch airshed, which may have been a potential source of heavy metals. However, as similar airborne metal ratios were found in stormwater runoff before the earthquakes, the demolition of the CBD can be eliminated as a pollution source for metals in this study.

**Table 5-4 The ratio of build-up per antecedent dry day ( $\mu\text{g}/\text{m}^2/\text{d}$ ) for different elements as a ratio to Cu (mean  $\pm$  SE) from each land-use area. Within each elemental group, those sharing a common letter are not significantly different ( $p > 0.05$ ); determined from a permutation MANOVA and subsequent multiple ANOVA's.**

Ratio to Cu	Ind	Res	Air
<i>Cu</i>	1	1	1
<i>Cr</i>	$1.0 \pm 0.1^a$	$0.7 \pm 0.1^b$	$1.2 \pm 0.2^a$
<i>Mn</i>	$1.7 \pm 0.1^a$	$1.34 \pm 0.1^a$	$2.5 \pm 0.2^b$
<i>Ni</i>	$0.1 \pm 0.009^a$	$0.1 \pm 0.01^a$	$0.2 \pm 0.01^b$
<i>Zn</i>	$5.4 \pm 0.4^a$	$5.0 \pm 0.4^a$	$5.6 \pm 0.5^a$
<i>Pb</i>	$0.5 \pm 0.04^b$	$0.3 \pm 0.03^a$	$0.3 \pm 0.01^a$
<i>As</i>	$0.2 \pm 0.01^a$	$0.2 \pm 0.02^a$	$0.2 \pm 0.02^a$
<i>Sb</i>	$0.03 \pm 0.003^a$	$0.03 \pm 0.003^a$	$0.03 \pm 0.003^a$



**Figure 5-2 Wind rose plots for each experimental site along a 120° transit line, where the x-axis represents the frequency (%) of occurrence**

### 5.3.5. Dry deposition rate

Meteorological and geometrical (including topographical) characteristics influence pollutant deposition. Topography and wind characteristics were thus monitored for each of the experimental sites. The Ind site consistently had higher pollutant loads compared to the Res and Air sites; this was attributed to Ind having different topography to the other sites. Ind was located at the base of a hill range (height approximately 400 m), see Figure 5-3. During a

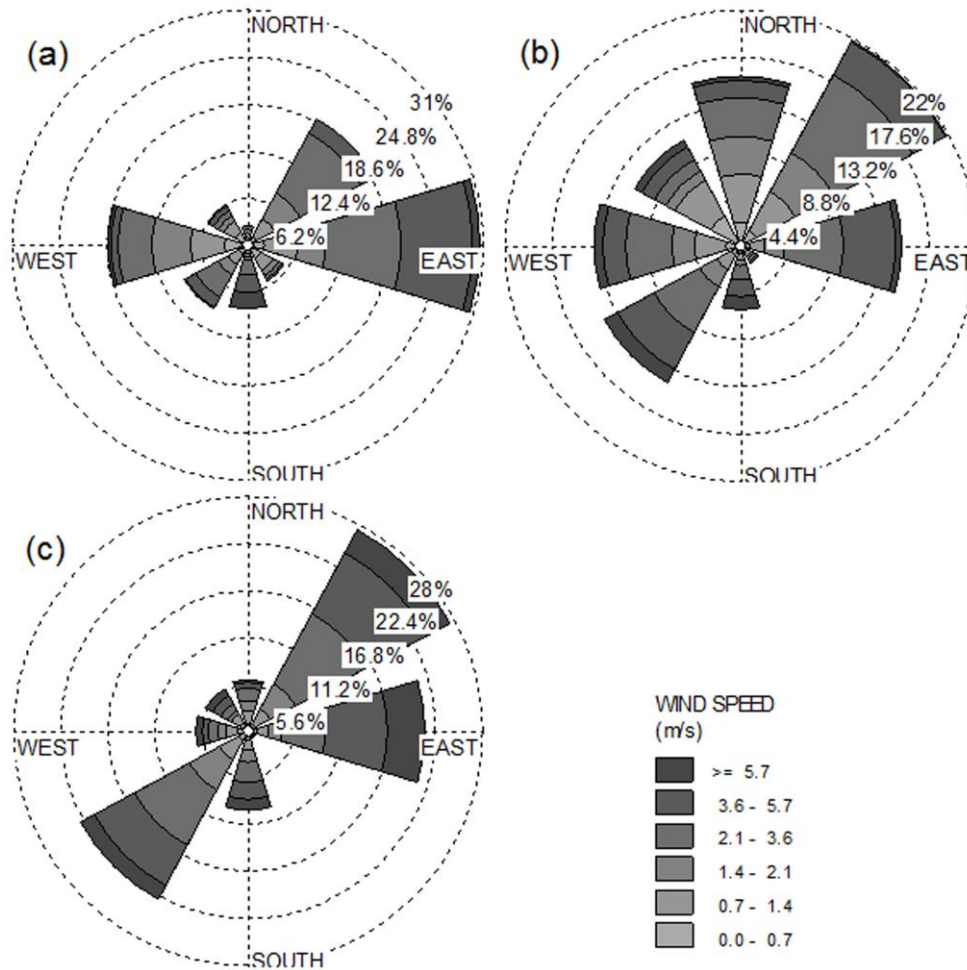
northerly and easterly wind, the Ind experimental site was located on the windward side of a slope where the dry deposition rate is promoted, unlike the other receptor sites (Air and Res) which were on a flat terrain. Furthermore, Ind only had light industry in its catchment, and thus, had no major sources of atmospheric heavy metal emissions, which could have influenced heavy metal deposition. In addition, some variation in deposition rates would have occurred at the Ind and Res testing sites due to the street canyon effect. The street canyon effect can alter the microclimate (i.e. wind vortices, local pressure, and ventilation), which can result in varying atmospheric pollution concentrations (Vardoulakis et al. 2003). As Res and Ind had buildings nearby unlike Air, it is possible that the dry deposition rate varied between the sites. However, the street canyon effect was minimised in Res and Ind by placing the boards in relatively open spaces.



**Figure 5-3 The Ind testing site was located next to a hill.**

Wind speed is an important controller of dry deposition, i.e. deposition decreases when wind speed decreases (Noll et al. 1988). Each receptor site had similar wind speed distributions (Figure 5-4); the wind speed range 2.1 – 3.6 m/s had the highest frequency of occurrence at all sites suggesting that wind speed patterns were not responsible for differences in pollutant deposition rates observed between sites. Wind speed can also influence the resuspension of particles from a surface following their deposition, although it is not as effective as mechanical stresses at resuspending materials (Sehmel 1980b). Increased resuspension is associated with an increase in wind speed with a large increase in the resuspension rate observed when wind speed exceeds 5 m/s for large particles ( $>22.1 \mu\text{m}$ ) (Nicholson 1993).

Wind speeds exceeding 5.7 m/s had a low frequency of occurrence in this study (5.3%, 3.9%, and 3.2% for Air, Ind, and Res, respectively); therefore, resuspension was unlikely to account for the different deposition loads in this study.



**Figure 5-4 Wind speed and wind direction for the (a) Ind (b) Air and (c) Res land-use areas from the period of January 2013 to December 2013. The wind rose plot indicates the frequencies of winds blowing from an angle to the experimental site and coded bands indicating the wind speed range**

### **5.3.6. Potential sources of atmospheric metals**

#### **5.3.6.1. Vehicular activity**

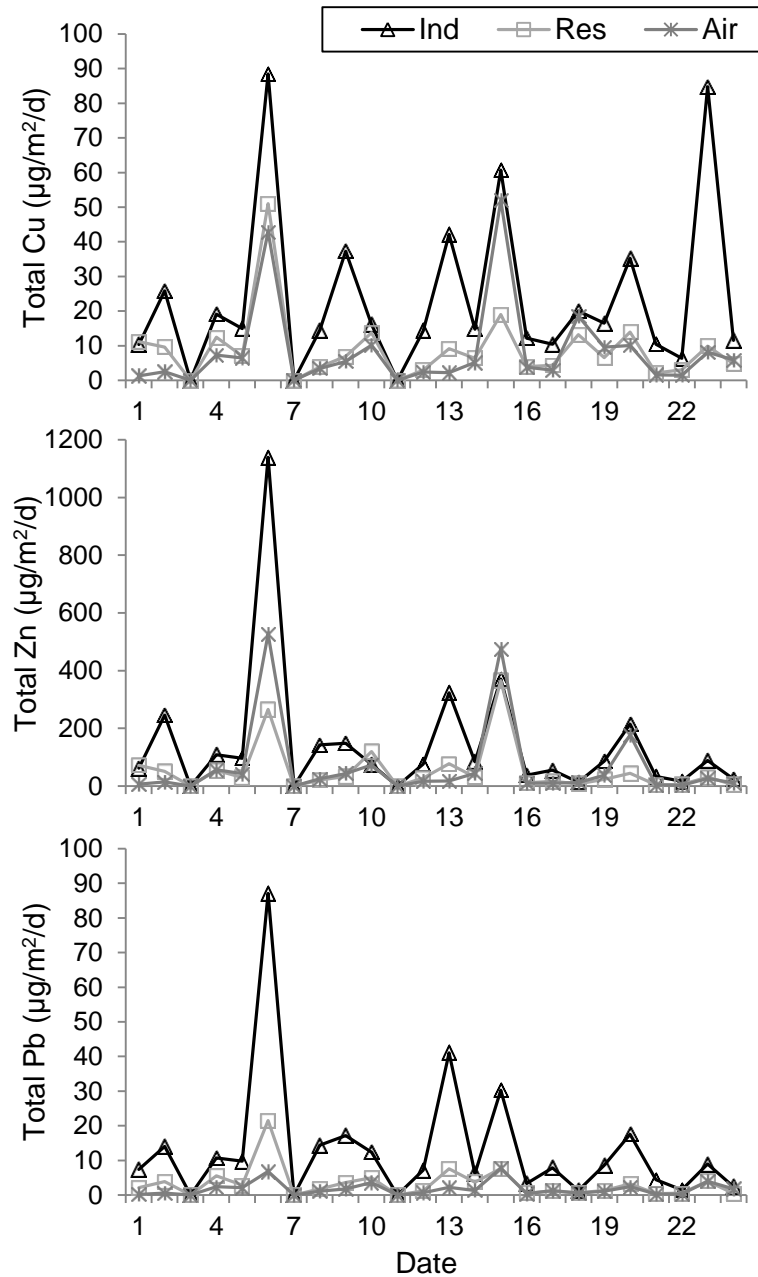
The similar pollutant ratios for each land-use area suggested that metal pollutants had the same origin. Davis and Birch (2011), found a consistent composition of metals from vehicular activity of 1:0.4:5.4 (Cu:Pb:Zn). Additionally, Moores et al. (2009) found similar ratios of total Cu to total Zn (4-5:1) in road runoff in two out of three sampling sites (the difference in other site was associated with either different traffic behaviours or particulate filtering). This contribution ratio was very similar to the ratios found in this study (Table 5-4), suggesting that vehicular activity was the dominant source of atmospherically deposited pollutants. Other studies have discussed the importance of vehicular activity to pollution loads (Chu-Fang et al. 2005; Conko et al. 2004; Hjortenkrans et al. 2007; Sternbeck et al. 2002). Particulates from vehicular wear and tear immediately become airborne which then undergo settling and dispersal processes (Bullin and Moe 1982). However, simply associating the pollutants origin to vehicular activity, in this instance, was questionable. Firstly, the Ind and Air sites were assumed to have a greater influence on the airborne metal concentrations, and hence deposition, than vehicular activity because of greater source emissions within their catchments (Huston et al. 2009; Motelay-Massei et al. 2005; Ray et al. 2012; Sartor et al. 1974). For example, Pb is commonly added to aviation fuel to inhibit valve seat recession (a major safety concern) and boost the octane number (US EPA 2008); therefore, higher concentrations of Pb from the airside site were expected. Secondly, the roads surrounding the receptor sites did not have similar characteristics, they had: different speed limits (50 km/h to 100 km/h); different braking situations (ranging from no required braking to slight/moderate deceleration); varying traffic densities; and different vehicle types (trucks and cars) predominantly using the roads. As road characteristics are known to strongly influence pollutant build-up (Kennedy and Gadd 2003), varying pollutant loading trends were expected. In particular, the main vehicle type on the road neighbouring Ind was trucks - car activity was typically limited to commuting times. As tyres have different weighted average for ZnO in the tread (the part exposed to wear) for a car (1.2%) and a truck (2.1%), it was assumed that the Zn loads from trucks would be higher than cars (Smolders and Degryse 2002). Similarly,

Garg et al. (2000) found that the airborne Cu emitted from brake pads ranged from 5.1 mg/mi to 14.01 mg/mi for small cars to large pickup trucks, respectively. Therefore, with varying quantities of Zn and Cu being released into the atmosphere from trucks and cars, different ratios of Zn to Cu were expected in Ind; however, this was not observed. Furthermore, higher PM<sub>10</sub> emissions were detected in Auckland, New Zealand, from heavy vehicles compared to light duty vehicles (Davy et al. 2011). Furthermore, the similar pollution loads observed between Air and Res did not conform to previous findings of pollutant fluxes rapidly decreasing with distance from a road, reaching background levels after 5 - 40 m (Pagotto et al. 2001; Harrison and Johnston 1985; Sutherland and Tolosa 2001). Air and Res had similar mean pollutant loads; however, the distances to their nearest roads were different. The airside site was 680 m from the point where airplanes touchdown on the runway, 30 m from the airside access roads, and 360 m from the nearest public road. The residential site was 40 m from the nearest road. Additionally, Moores et al. (2009) observed different vehicle emission factors from roads with differing traffic behaviours: total Cu varied from 0.09 to 0.05 mg/vehicle/km depending on whether the traffic was interrupted (e.g. intersections) or free flowing; similarly, total Zn varied from 0.62 to 0.28 mg/vehicle/km. As the Res site was located near a traffic-light controlled intersection, higher Cu and Zn loads were expected in runoff in comparison to the Air site that had free moving traffic at the nearby road. Therefore, if vehicular activity was the source of metals, then Air should have lower metal loads, which was not observed.

Pollution trends of increasing/decreasing loads (per antecedent dry day) between the three receptor sites were remarkably similar throughout the year, as exemplified in Figure 5-5, providing further evidence that vehicular activity does not appear to be the dominant source of Cu, Pb, and Zn. Since Cu and Pb are related to traffic congestion, and Zn is related to traffic volume (Gunawardena et al. 2013) varying trends would likely occur between the sites when traffic conditions differ. For example, the road usage neighbouring Res would be expected to change during certain periods (e.g. academic holidays (Dec-Feb) since the Res area incorporated a large University) without the other sites changing, yet this was not observed. Similarly, Tippayawong et al. (2006) also found no relationship between air pollution and vehicular activity in Chiang Mai, Thailand; particle number concentration did



not vary with traffic patterns and volumes - this result was unexpected as there were over one million registered motorcycles in the city.



**Figure 5-5 Total Cu, Zn, and Pb loads per antecedent dry day from February to December 2013. The results indicate no temporal variability throughout the 11 month period.**

#### 5.3.6.2. *Other sources*

Christchurch is known to have an air quality pollution problem and much research has been conducted on smoke, PM, SO<sub>2</sub>, and CO concentrations (Corsi et al. 2006; Scott and Sturman 2006; Spronken-Smith et al. 2002; Sturman 1985; Wilson et al. 2006); however, research on atmospheric heavy metal concentrations is lacking. Thus, characterising the source of heavy metal pollutants is difficult. The methodology used in this research does not allow for the source of heavy metals to be identified, instead the source can only be suggested by conducting a literature review. It is recommended that a source appointment study be undertaken to characterise the source of atmospheric heavy metals in Christchurch.

A potential source of metal pollutants conveyed in the atmosphere is from transboundary pollution, likely originating from Australia. Australia is reportedly the largest contributor of dust in the southern hemisphere (Marx et al. 2008), which is greatest during the late-summer and autumn seasons as more fine particulates are available for transport due to the abatement of river flows and lack of vegetation preventing Aeolian entrainment (Marx et al. 2005a). The annual mean transport rate of Australian dust to New Zealand is 3.7 – 6.9 µg/m<sup>3</sup> (Marx et al. 2005a). This dust scavenges atmospheric heavy metals, particularly Cu and Pb, as they traverse over the urban and/or industrial areas on Australia's eastern seaboard (Marx et al. 2005b; Marx et al. 2008). Marx et al. (2005b) found persistent elevated concentrations of atmospherically deposited Cu and Pb, among others, from the remote alpine regions of New Zealand, which was associated with long-travelled dust from Australia. Marx et al. (2008) determined that the annual variability of atmospheric metal concentrations in New Zealand associated with Australian dust was 0.293 - 0.6 ng/m<sup>3</sup>, 0.5 – 0.9 ng/m<sup>3</sup>, and 0.4 - 0.8 ng/m<sup>3</sup> for Pb, Zn, and Cu respectively. Although the majority of Australian dust will probably deposit on the West Coast of the South Island due to the orographic effects of the Southern Alps, it cannot be ruled out as a source of particulate matter and trace elements in the eastern side of New Zealand, including Christchurch (Marx et al. 2005b; Marx et al. 2008). Additionally, heavy metals carried in air masses independently of dust can significantly increase the Australia to New Zealand metal flux (Marx et al. 2008). The long-range transport of metals

from Australia to New Zealand may be playing a vital role in the atmospheric chemistry and the biogeochemistry of New Zealand (Marx et al. 2005a).

Another potential source of atmospheric metals may be soil erosion from the Port Hills (a hill range adjacent to Christchurch). A soil sample from the Port Hills (located near the Ind testing site – S43 34.857 E172 41.027) was taken and analysed for total Cu, Zn, and Pb using the APHA (2005) Method 3030F. The soil sample contained 18.3 µg/g, 94.1 µg/g, and 10.1 µg/g of Cu, Zn, and Pb, respectively. Therefore, soils erosion from the Port Hills may be a potential source of atmospheric metals in Christchurch. However, as most of the Port Hills slopes are covered with grassland, it was assumed that soil erosion from wind action was minimal. Other potential pollutant sources could include aged aerosols, fugitive dust, and domestic heating (Scott 2005), although, these were not investigated as part of this research.

#### **5.4. Conclusion**

This study found that irrespective of land use area, similar pollutant trends were measured in atmospheric deposition throughout a year of monitoring. Although the Ind site had consistently higher pollutant loads than the other land-use areas, this was attributed to its local topography (located at the base of hills) rather than land-use activity. Wind speed or potential pollutant resuspension did not appear to greatly influence pollutant dry deposition rates since all land-use areas had similar wind speed characteristics as well as similar temporal pollutant trends. Ratios of different heavy metals to Cu were relatively homogeneous between areas, suggesting that pollutants originate from a similar source(s). Although the metal composition ratio indicated that vehicular activity could be the dominant source of atmospherically deposited pollutants, roads surrounding the sites experienced different traffic behaviours but their pollutant trends remained similar. It is possible that a potential source of metals in the atmosphere comes from transboundary pollution originating in Australia, which is known to be a persistent source of atmospheric Cu and Pb to the remote alpine regions of New Zealand. Given the inherent complexities of meteorological influences and pollutant dynamics in any land-use area, it is difficult to definitively state the origin of atmospheric pollutants, although,

this study has helped address the poorly understood phenomenon in the context of stormwater pollutant loads. Implications of this study could help stormwater managers in optimising pollutant reduction (i.e. source control) strategies within their catchments.

# Chapter Six:

## Modelling Airborne Pollutant Loadings in Stormwater Runoff

## **6. MODELLING AIRBORNE POLLUTANT LOADS IN STORMWATER RUNOFF**

### **6.1. Introduction**

#### ***6.1.1. Urban stormwater quality modelling***

Knowledge of stormwater pollution loads (or concentrations) throughout rain events is required to evaluate the impact of stormwater on the health and the ecology of an urban waterway. This knowledge is also required to help select appropriate stormwater attenuation and treatment infrastructure and to determine the effectiveness of existing stormwater management strategies (Vaze and Chiew 2003a). Thus, stormwater models are increasingly being relied on as an aid to inform solutions to stormwater quality problems in the urban environment (Obropta and Kardos 2007). They are an indispensable prediction tool when optimising mitigation and management measures for waterways protection (Egodawatta and Goonetilleke 2008b; Vaze and Chiew 2003a). Additionally, stormwater models can be integrated into a stormwater quality monitoring campaign which subsequently can continue to provide information on the analysed system after the monitoring campaign is concluded (Birch et al. 2013). Typically, either “process-based” stormwater models (Egodawatta et al. 2009; Huber and Dickinson 1988; Wang et al. 2011; Wicke et al. 2010) or regression models (Driver and Tasker 1990; Irish et al. 1998; Jewell and Adrian 1982) are used to estimate pollutant loads in stormwater runoff (Vaze and Chiew 2003a).

#### ***6.1.2. Process-based models***

Process-based stormwater models simulate pollutant build-up and the subsequent pollutant wash-off as two distinct processes (Vaze and Chiew 2003a). Whereby, pollutant build-up describes the accumulation of pollutants on an impermeable surface during antecedent dry days; pollutant wash-off describes the removal of pollutants by the shear stress generated by surface runoff flow and the energy imparted by the falling precipitate (Vaze and Chiew 2002).

The processes controlling pollutant build-up and wash-off are discussed in Table 6-1. Pollutant build-up assumes that all dry weather processes (e.g. local traffic flow, airborne resuspension, and street cleaning processes) affect pollutant accumulation, which subsequently washes-off during a rain event (Sartor and Boyd 1972). Pollutant accumulation is not a linear function of antecedent dry days because the pollutants will resuspend into the atmosphere, and therefore, the rate of pollutant build-up ( $\text{g day}^{-1}$ ) declines over the dry period until reaching a maximum holding capacity (Opher and Friedler 2010; Auckland Regional Council 2005). Pollutant wash-off is controlled by the turbulence generated by the rainfall and the shear stress transmitted by the flowing water loosening pollutants from a surface, which are subsequently carried away in runoff (Vaze and Chiew 2003b). However, it is believed that most storm events cannot remove the total pollutant load from typical asphalt or concrete urban surfaces (Vaze and Chiew 2002, 2003b). Only a limited amount of the available pollutant load (free-load) is removed during a rain event, the remaining pollutants (fixed-load) are entrapped to varying degrees by the impermeable pavement surface (Vaze and Chiew 2002). Similarly, Egodawatta et al. (2009) found that only 75% of the total pollutant load was removed from a roof surface when the rain intensity was 20 mm/h and only during a 115 mm/h rain event was almost all of the available pollutant load removed.

The physical processes controlling pollutant build-up and wash-off can be modelled using mathematical equations with varying coefficients reflecting particulate loads and build-up rates (Egodawatta et al. 2009). For example, the pollutant build-up function (eq. 6-1) can be described by a power equation of antecedent dry days (Egodawatta et al. 2009) and the wash-off function can be described by an exponential decline equation of rainfall intensity and time (eq. 6-2) (Egodawatta et al. 2007; Egodawatta and Goonetilleke 2008b; Egodawatta et al. 2009). The models can be calibrated for different sites or scenarios by adjusting the coefficients to best reflect the data collected.

$$B = aD^b \quad \text{eq. 6-1}$$

$$F_w = W/W_0 = C_f(1 - e^{-kIt}) \quad \text{eq. 6-2}$$

Where  $B$  = build-up load ( $\text{mg}/\text{m}^2$ );  $a$ ,  $b$  = empirical coefficients;  $D$  = antecedent dry days;  $F_w$  = fraction wash-off;  $W$  = weight of the pollutant mobilised after time  $t$ ;  $W_0$  = initial weight of pollutant;  $C_f$  = capacity factor;  $k$  = wash-off coefficient;  $I$  = rainfall intensity;  $t$  = time (h).

However, different process-based models assign varying importance to certain pollutant build-up and wash-off variables (Table 6-1). For example, antecedent dry days is an essential variable in the SWMM model, but it is not taken into account in the MOSQUITO model (Deletic and Maksimovic 1998). Similarly, there is a diversity of opinions regarding which explanatory variables control pollutant wash-off dynamics (Vaze and Chiew 2003a). For example, Wicke et al. (2010) had runoff rate as the explanatory variable controlling pollutant wash-off of atmospheric pollutants from urban surfaces, whereas, Egodawatta et al., (2008a) had rain intensity and duration as the explanatory variables.



**Table 6-1 The influencing variables of pollutant build-up and wash-off dynamics.**

	<b>Variable</b>	<b>Description</b>
<b>Pollutant build-up</b>	<i>Antecedent dry days</i>	The gradual accumulation of pollutants amid the dry period before a rain event (Soonthornnonda and Christensen 2005).
	<i>Dry deposition</i>	The direct settling of pollutants from the atmosphere to an impermeable surface. Dry deposition processes are especially important in urban centers where atmospheric pollutant concentrations are the highest (Lu et al. 2003).
	<i>Resuspension</i>	The re-entrainment of previously deposited pollutants into the atmosphere (Nicholson 1988). Resuspension can be a function of wind (Nicholson 1988) or vehicle induced turbulence (Patra et al. 2008).
	<i>Land-use activity</i>	Land-use activities can significantly alter pollutant accumulation on an impermeable surface (Chow et al. 2013); even within the same land-use, pollutant build-up can be highly variable (Liu et al. 2011) depending on the surface properties and the activities that occur in that area.
	<i>Cleaning practices</i>	Cleaning practices, either intentional (street sweeping) or by rainfall, remove accumulated pollutants. Typically, commercial areas have lower pollutant loads than the mean for cities on a whole due to the increased frequency in which they are cleaned (Sartor and Boyd 1972).
<b>Pollutant wash-off</b>	<i>Rain depth</i>	Pollutant wash-off increases with rain depth as more pollutants are removed by the sheer stress imparted by surface flow (Vaze and Chiew 2003b).
	<i>Rain intensity</i>	Pollutant wash-off increases with rainfall intensity as more particulates are mobilised from a surface (Barrett et al. 1995). This is due to the energy input from falling raindrops removing more particulates (Duncan 1995).
	<i>Rain duration</i>	Pollutant wash-off is likely to continually increase with duration as some pollutants will be removed throughout the rain event (Opher and Friedler 2010). However, the rate of pollutant wash-off is expected to decline exponentially with time as the available pollutant load on a surface decreases (Vaze and Chiew 2002).
	<i>Rain volume</i>	Rain volume is typically described as a poor indicator of pollutant concentrations but it is an important indicator of pollutant loads (Barrett et al. 1995). This is due to larger storms diluting the runoff and thus lowering the concentration of pollutants. However, they do increase the total mass of pollutants that are washed from a surface (Opher and Friedler 2010) from the shear stress generated by flow (Duncan 1995).
	<i>Runoff rate</i>	Runoff rate is influenced by the rainfall distribution, i.e. how the rainfall intensity varies over the rain event (NJDEP 2004).
	<i>Runoff volume</i>	Runoff volume is influenced primarily by the total rainfall amount, catchment drainage area, and percentage impervious cover (Brezonik and Stadelmann 2002). As impervious surfaces have a very high runoff coefficient, rain and runoff volume can be used interchangeably for qualitative analysis (Opher and Friedler 2010).

### **6.1.3. Regression models**

Regression models fit a line to the average relationship between a dependent variable and one or more independent variables (eq. 6-3), assuming that the variation in the dependent variable can be explained scientifically by quantitative changes in the independent variables that govern the process (Irish et al. 1998). In stormwater modelling, the regression equation combines the variables controlling pollutant build-up and pollutant wash-off processes (Table 6-1) into a single unified equation, unlike process-based models that represent build-up and wash-off as separate processes.

$$Y_i = (b_0 + b_1X_{1i} + b_2X_{2i} + \dots + b_nX_{ni}) + \varepsilon_i \quad \text{eq. 6-3}$$

Where,  $Y_i$  = outcome variable;  $b_0$  = intercept of the line;  $X_1, X_2 \dots X_n$  = predictor variables;  $b_1, b_2 \dots b_n$  = regression coefficients;  $\varepsilon_i$  = error.

### **6.1.4. Process-based models versus regression models**

Process-based models are superior to regression models for understanding the scientific relationship between factors and for better representing the physical processes behind pollution build-up and wash-off in the real world (Aryal et al. 2009). However, the benefit of using process-based models over regression models for prediction is ambiguous, i.e. it is unclear if the additional time and effort to calibrate process-based models yields better predictive results (Vaze and Chiew 2003a). Lindner-Lunsford and Ellis (1987) found that when simulating stormwater pollutant loads, there was no discernible difference in accuracy between a process-based (conceptual) and a regression model and that neither model was capable of accurately simulating stormwater loads. Therefore, choosing which model to use becomes a question of context based on the type of predictions required and whether the more detailed results obtained from a process-based model justifies the added cost and time needed to produce them (Lindner-Lunsford and Ellis 1987). Both types of models have difficulties in accurately predicting stormwater quality modelling because quality models involve many

highly uncertain variables. This explains why stormwater quality models are inferior to stormwater quantity models (Obropta and Kardos 2007). For example, any advancement of stormwater quality models is hindered by the complexity and dynamic nature of stormwater pollution (Beck and Birch 2013). In addition, the accuracy of stormwater quality modelling is limited by the lack of event water quality data and the inconsistent pollutant concentration data that is in literature (Duncan 1995). Other deficiencies in stormwater quality modelling are: incomplete water quality data on complete storms (Deletic and Maksimovic 1998); not fully reliable water quality data due to the low accuracy in measurement; different quality assurance methods for monitoring; and deficient frequency of data collection, i.e. the time between collecting samples is inadequate to correctly record extreme storms (Deletic and Maksimovic 1998). Furthermore, determining which explanatory variables to include into the model is complicated by the myriad of conflicting information on pollutant build-up and wash-off dynamics, as illustrated in Table 6-3. Typically, a relationship between antecedent dry days and pollutant loads is observed. However, there is no consensus on which variable(s) control pollutant wash-off. This is further complicated as different pollutants can have different relationships with the explanatory variables. For example, Deletic and Maksimovic (1998) found a relationship between TSS and runoff volume, runoff rate, and rainfall intensity but did not find a relationship between TSS and antecedent dry days. Conversely, conductivity was found to have a relationship with antecedent dry days but not with the pollutant wash-off explanatory variables. Similarly, Wang et al. (2013) found that total nitrogen (TN) was related to antecedent dry days but chemical oxygen demand (COD), TSS, and total phosphorous (TP) were not related, instead, COD, TSS and TP were related to rain intensity. TSS and TP were also related to rain duration. Additionally, formulating models under the assumption that pollutant processes are consistent within the same land-use can be inaccurate since this approach does not consider localised pollutant build-up dynamics (Liu et al. 2013). Therefore, pollutant build-up and wash-off dynamics are complex, site-specific and a single model may not be applicable to all situations. However, regression models can overcome this difficulty as customising models for different situations is relatively simple and quick. For example, independent models for individual pollutants and for different land-use conditions can be developed based on monitoring data for those conditions. A particular advantage of regression modelling is that the uncertainty associated with the inputted

variables is also represented in the model (Zoppou 2001). In addition, regression models are a useful tool in identifying pollutant specific casual variables (Irish et al. 1998), i.e. determining which independent variable(s) influence specific pollutants loads.

Nonetheless, a disadvantage of regression models is that they cannot accurately predict outside their calibration range. Therefore, it is more important to calibrate a regression model with a full range of storm events (Lindner-Lunsford and Ellis 1987). Additionally, regression models are very site-specific. Due to these short-comings, regression models can be used only for preliminary analysis of stormwater data or in situations where process-based model approaches cannot be used (Zoppou 2001). A summary of regression models versus process-based models is exemplified in Table 6-2.

**Table 6-2 Process-based models versus regression models.**

	<b>Process-based models</b>	<b>Regression Models</b>
<i>Method</i>	<ul style="list-style-type: none"> <li>• Separate build-up and wash-off models</li> </ul>	<ul style="list-style-type: none"> <li>• Combined build-up and wash-off model</li> </ul>
<i>Output</i>	<ul style="list-style-type: none"> <li>• Mathematical equations with varying coefficients reflecting specific site conditions</li> </ul>	<ul style="list-style-type: none"> <li>• Fitted linear line to average relationships between variables</li> </ul>
<i>Advantages</i>	<ul style="list-style-type: none"> <li>• Provides better scientific understanding of the relationships between the explanatory variables and pollutant build-up and wash-off dynamics</li> </ul>	<ul style="list-style-type: none"> <li>• Easy to customise to different sites,</li> <li>• Determines the relationships between pollutant loads in runoff and the casual variables</li> </ul>
<i>Limitations</i>	<ul style="list-style-type: none"> <li>• Requires additional time and effort to calibrate,</li> <li>• Explanatory variables are preselected,</li> <li>• Difficulty in accurately predicting stormwater quality</li> </ul>	<ul style="list-style-type: none"> <li>• Model is very site-specific,</li> <li>• Cannot predict outside its calibration range,</li> <li>• Difficulty in accurately predicting stormwater quality</li> </ul>

**Table 6-3 Relationships between meteorological characteristics and runoff quality in process-based and regression models.**  
**Where: “x” represents non-significant relationships; “Y” represents significant relationships; and “-” represents relationships not discussed in the studies.**

Study Area	Author	Location	Parameters studied	ADD	Rd	RI	Dur	Vol	Ru. Vol	Ru. Rate
Applied pollutants	Vaze and Chiew (2003b)	Melbourne, Australia	TSS & TP	-	-	Y	-	-	Y	-
Roads	Barrett et al. (1998)	Texas, U.S.	TSS	-	-	Y	-	-	Y	-
	Berhanu Desta et al. (2007)	Ireland	TSS	x	x	Y	x	-	x	-
	Crabtree et al. (2006)	U.K.	Metals & PAHs	x	x	Y	x	-	-	-
	Deletic and Maksimovic (1998)	Sweden & former Yugoslavia	TSS Cond.	x Y	-	Y x	-	-	Y	Y x
	Vaze and Chiew (2002)	Melbourne, Australia	Sediment loads	Y	-	-	-	-	-	-
	Ellis et al. (1986)	U.K.	Sediments & metals	-	-	-	Y	-	-	-
	Ellis and Harrop (1984)	U.K.	Sediment loads	Y	-	Y	Y	Y	-	-
	Gan et al. (2008)	Guangzhou, China	Metals, COD, OP, & O&G	Y	Y	x	x	-	-	-
	Han et al. (2006)	Los Angeles, U.S.	Cond., hard., COD, DOC, TSS & KN	Y	Y <sup>1</sup>	x	x	-	-	-
	Harrison and Wilson (1985)	U.K.	Pb	x	-	-	-	-	-	Y
	Hewitt and Rashed (1992)	U.K.	Pb <sup>2</sup>	Y	-	-	-	-	-	Y
	Kayhanian et al. (2003)	California, U.S.	Sediments, pH, T, metals, nutrients, major ions, microbes, pesticides	Y <sup>3</sup>	Y <sup>3</sup>	Y <sup>3</sup>	-	-	-	-
	Khan et al. (2006)	California, U.S.	O&G	Y	Y	-	x	-	-	-
	Opher and Friedler (2009)	California, U.S.	Cr, TOC Pb, Zn, TSS	Y Y	-	Y	-	Y	-	-
Impervious surfaces	Haster and James (1994)	Austin, U.S.	SS	Y	-	-	-	-	-	Y
Commercial carpark	Hoffman et al. (1982)	San Francisco, U.S.	O&G	x	Y	-	-	-	-	-
Roofs	Yaziz et al. (1989)	Selangor, Malaysia	T, pH, coliforms, turbidity, plate counts, Zn, & Pb	Y	-	Y	-	-	-	-
	Rocher et al. (2004)	Paris, France	PAHs, n-alkanes & metals	Y	Y	x	x	-	-	-
	Egodawatta et al. (2009)	Gold Coast, Australia	PM	Y	-	Y	Y	-	-	-

Study Area	Author	Location	Parameter's studied	ADD	Rd	RI	Dur	Vol	Ru. Vol	Ru. Rate
Roofs	Charbeneau and Barrett (1998)	Austin, U.S.	EMC (TSS)	x	-	-	-	-	Y	-
	Wang et al. (2011)	L.A. County, U.S.	KN, TSS, Zn & Cu	Y	-	-	-	-	Y	-
	Robien et al. (1997)	Bayreuth, Germany	TSS & metals	Y	-	-	-	-	Y	-
CSOs	Gupta and Saul (1996)	U.K.	First flush (TSS)	Y	-	Y	Y	-	-	-
Atm. dep.	Gunawardena et al. (2011)	Gold Coast, Australia	PM in dry dep. PM in bulk dep.	Y x	x Y	-	-	-	-	-
	Wicke et al. (2012a)	Christchurch, N.Z.	TSS and metals	Y	-	-	-	-	-	-
	Tanner and Wong (2000)	Hong Kong, China	Metals	-	Y	-	-	-	-	-
	Hu and Balasubramanian (2003)	Singapore, Malaysia	Metals	-	-	-	-	Y	-	-
	Takeda et al. (2000)	Higashi-Hiroshima, Japan	Metals	-	-	-	-	Y	-	-
Urban runoff (commercial /residential roofs and roads)	Wang et al. (2013)	Chongqing, China	EMC & PLPC (COD) [in 1 of 4 sites]	x	x	Y	x	-	-	-
			EMC & PLPC (TSS) [in 1 of 4 sites]	x	x	Y	Y	-	-	-
			EMC (TSS) [in 1 of 4 sites]	x	x	Y	Y	-	-	-
			EMC & PLPC (TP) [in 1 (RI) and 2 (Dur) of 4 sites]	Y	x	x	x	-	-	-
			EMC & PLPC (TN) [in 1 of 4 sites]	Y	x	x	x	-	-	-

Where: ADD = antecedent dry days, RD = rain depth, RI = rain intensity, Dur = rainfall duration, Vol = rainfall volume, Ru. Vol = runoff volume and Ru. Rate = runoff rate, VSS = volatile suspended solids, KN = kjeldahl-N, DOC = dissolved organic carbon, PLPC = pollution load producing coefficients; CSOs = Combined Sewer Overflows; cond. = conductivity; hard. = hardness; <sup>1</sup>correlations found for most pollutants but for which pollutants was not stated; <sup>2</sup>correlations found for Pb only; <sup>3</sup>correlations found for: 23 of 24 models (ADD), 23 of 25 models (RD), and 7 of 11 models (RI).

#### ***6.1.5. Modelling airborne pollutant loads in stormwater runoff***

Atmospheric deposition has been acknowledged as an important source of heavy metals to urban runoff (Gunawardena et al. 2013; Huston et al. 2009; Sabin et al. 2005, 2006; Wicke et al. 2012b), as discussed in Section 2.2. However, few studies have modelled the effects of atmospheric deposition as a source of heavy metals in stormwater pollution; therefore, many uncertainties and challenges remain with managing these airborne pollutants in runoff. Wicke et al. (2010) modelled atmospherically derived pollutants in stormwater runoff using process-based models. Antecedent dry period was used as the defining variable for pollutant build-up while runoff rate explained pollutant wash-off. The model was found to replicate the experimental values well and was very informative for determining the controls that affect airborne pollutant build-up and wash-off. However, pollutants were washed-off by simulated rainfall which does not take into account the variability throughout a rain event (e.g. rain intensity), nor does it consider wet deposition. As wet deposition is considered an important component of bulk deposition (Morselli et al. 2003), measuring both wet and dry deposition is crucial in order to model catchment-wide atmospheric deposition loads in runoff (Davis and Birch 2011).

The objective of this research was to develop an event-process driven stormwater quality model that can estimate bulk atmospheric deposition loads for total Cu, total Zn, total Pb, and TSS from three different land-use areas: residential, industrial, and airside (as previously discussed in Chapter 5). As stormwater runoff was collected from modular concrete boards, the factors that confound typical stormwater models, such as sewer sediment transport and microbial degradation, were not present. Therefore, a simplified model on bulk deposition loads in stormwater was generated. In addition, this research aimed to identify the casual variables influencing airborne pollutant build-up and wash-off in stormwater runoff. Knowledge of the mechanisms of pollutant build-up and wash-off is an essential component of stormwater modelling (Nazahiyah et al. 2007). Improving the accuracy of stormwater modelling will lead to better understanding of local stormwater quality, and thus, increase the appropriateness of selected treatment systems (Liu et al. 2013).

## 6.2. Materials and Methods Overview

The data obtained for analysing the spatial variability of Cu, Pb, Zn, and TSS loads in runoff from different land-use areas (Chapter 5) was used to model atmospherically derived stormwater pollution. Data on atmospheric humidity (Rh), pressure (P), and temperature (T) was obtained from the National Institute of Water & Atmospheric Research (NIWA) main weather station in Christchurch.

### 6.2.1. *Analysis of pollutant build-up and wash-off*

#### 6.2.1.1. *Mixed-effect models*

Mixed-effect prediction models for the combined build-up and wash-off of total Cu, total Zn, total Pb and TSS (dependent variables) in the Air, Ind, and Res land-use areas were generated. Mixed-effect models are a form of a regression model that contains both fixed and random effects. In this study, the fixed effects were the independent meteorological variables (typically included in stormwater quality models) and the random effects were attributed to runoff collected from the concrete boards (unique to this research). Mixed-effect models are a flexible and powerful statistical tool for analysing replicated blocked design data (Pinheiro and Bates 2000).

#### 6.2.1.2. *Data inputted to the model*

Different meteorological variables were chosen as the independent (causal) variables, as presented in Table 6-4. The independent variables were analysed in their original scales and with various transformations applied (Table 6-5). Transformations were used to improve the accuracy of the model and to create linear relationships with the dependent variables. The log transformation fits the data to an asymptotic distribution, i.e. pollutant loads increase rapidly at the start of a rain event (or dry period) but as the rain event progresses the rate of pollutant



increase slows. The exponential transformation describes the rate of pollutant wash-off as slow at the beginning of a rain event but the rate increases as the rain event progresses. The arctan transformation fits the data to a cumulative distribution, i.e. pollutant loads increase rapidly at the beginning of an antecedent dry period, finally plateauing after 7 - 9 days. Wind direction (WD) had a sine and cosine transformations applied, i.e. the Fourier approximation, to linearise wind direction within the model.

For all the models generated, the dependent variables were log transformed to achieve normality of residual and stability in the error variance (Driver and Tasker 1990). The log transformation is suitable for stormwater quality modelling because there is typically more uncertainty with larger storm events, which if untransformed, results in heteroscedasticity and an invalid model (Driver and Tasker 1990).

**Table 6-4 Meteorological variables used for regression analysis.**

Independent variable	Abbreviation	Scientific significance in the model
Rain depth (mm)	RD	RD, RI, and Dur are (potentially) important controllers of pollutant wash-off (refer to Table 6-1 for more details)
Peak hourly rain intensity over the duration of the rain event (mm/h)	RI	
Rain duration (h)	Dur	
Antecedent dry days (d)	ADD	Pollutants build-up quickly at the start of an antecedent dry period; however, the build-up rate slows down after several days (Opher and Friedler 2010).
Median atmospheric pressure before rain (hPa)	P	Atmospheric pressure is co-dependent on wind speed and temperature (Wooten 2011). Therefore, it was used as an alternative variable explaining dry deposition rates.
Median relative humidity before rain (%)	Rh	High humidity promotes the hygroscopic growth of particle, which significantly increases dry deposition rates (Chen et al. 2012).
Median temperature before rain (°C)	T	Temperature influences humidity, which alters dry deposition rates (Chen et al. 2012).
Mean wind speed before rain (m/s) Mean wind speed during rain (m/s)	WS <sub>1</sub> WS <sub>2</sub>	Higher wind speeds increases the efficiency of particles to deposit onto a surface (Erisman and Draaijers 2003).
Mean wind direction before rain (radians) Mean wind direction during rain (radians)	WD <sub>1</sub> WD <sub>2</sub>	Dispersal patterns of pollutants are dependent upon the local wind direction conditions.

**Table 6-5 Transformations applied to the independent variables.**

Variable	Transformation applied
ADD	Arctan, logarithmic (base 10), & exponential
RD	Logarithmic (base 10) & exponential
RI	Logarithmic (base 10) & exponential
Dur	Logarithmic (base 10) & exponential
P	None
Rh	None
T	None
WS <sub>1</sub> , WS <sub>2</sub> ,	Vector function (e.g. $U_1 = -WS_1 * \text{Sine}(WD_1)$ & $V_1 = -WS_1 * \text{Cosine}(WD_1)$ )
WD <sub>1</sub> , WD <sub>2</sub>	Sine & Cosine

#### 6.2.1.3. *Data management*

Any significant outliers were removed from the data set. Outliers were determined using Cook's Distance. Cook's Distance determines if a datum exerts undue influence over the predicting parameters; therefore, if not removed the influencing datum may affect the model's ability to predict all data (Field 2013). Outliers may result from initially including a marginal datum, or from an unusual phenomenological event (Jewell and Adrian 1982). The models were calibrated against 85% of the pollutant load data and the modelled loads were then compared to the remainder of the pollutant load data for model validation (as recommended by Mourand et al. (2005)). Models were fitted using the lme4 package (Bates et al. 2014) within R version 3.1.0 (R Core Team 2014). The 'best' parsimonious model, i.e., the model that can explain most of the variation with the fewest variables inputted into the model, was determined using the lowest Akaike Information Criterion (AIC) values (Akaike 1998). The conditional and marginal goodness of fit,  $R^2_{(c)}$  and  $R^2_{(m)}$ , was determined using the method detailed in Nakagawa and Schielzeth (2013).  $R^2_{(m)}$ , describes the variance explained by the fixed factors, and  $R^2_{(c)}$ , describes the variance explained by the fixed (meteorological variables) and random (concrete board) factors (Nakagawa and Schielzeth 2013). For situations when the  $R^2_{(m)}$  and  $R^2_{(c)}$  are identical or similar, the random factor (concrete board) did not have an effect on the model. All the significance of the covariates (p-value < 0.05) in each model was confirmed using the "lmerTest" package (Kuznetsova et al. 2014).

### 6.3. Results and Discussion

#### 6.3.1. *Summary of input data*

A summary of the weather characteristics represented during the sampling campaign are shown in Table 6-6. The mean total heavy metal loads (Cu, Pb, and Zn) and TSS loads were measured in runoff from all three sampling areas are exemplified in Table 6-7. As regression models cannot accurately predict outside their calibration range, it was imperative to calibrate the model with a full range of storm events (Lindner-Lunsford and Ellis 1987). The mean

total heavy metal loads (Cu, Pb, and Zn) and TSS loads measured in runoff from all three sampling areas are exemplified in Table 6-7. Air and Res had similar pollutant loads to each other (excluding TSS), whereas, higher pollutant loads were found in Ind. The higher pollutant loads found in Ind were associated with variations in local topography rather than the activities that occurred in each area which were deemed insignificant (as discussed in Chapter 5).

**Table 6-6 Range of weather conditions represented during the sampling campaign, where n is the number of rain events sampled.**

	Ind (n = 28)	Res (n = 28)	Air (n = 25)
<i>ADD (d)</i>	0 – 21	0 – 21	0 – 27
<i>RD (mm)</i>	0.6 – 51.4	1 – 42.8	1.1 – 40.2
<i>RI (mm/h)</i>	0.2 – 6.4	0.4 – 10.2	0.6 – 4.5
<i>Dur (h)</i>	2.0 – 35.0	3.0 – 40.0	3.0 – 43.1
<i>WS<sub>1</sub> (m/s)</i>	0.04 – 2.4	0.4 – 3.1	0.2 – 2.2
<i>WS<sub>2</sub> (m/s)</i>	0.2 – 7.7	0.4 – 8.1	0.2 – 6.9

**Table 6-7 Summary of total Cu, Zn, Pb and TSS loads in runoff (mean  $\pm$  S.E.).**

	Total Cu ( $\mu\text{g}/\text{m}^2$ )	Total Zn ( $\mu\text{g}/\text{m}^2$ )	Total Pb ( $\mu\text{g}/\text{m}^2$ )	TSS ( $\text{mg}/\text{m}^2$ )
<i>Ind</i>	$87.8 \pm 6.8$	$505.2 \pm 63.0$	$49.9 \pm 4.7$	$364.3 \pm 33.6$
<i>Res</i>	$36.8 \pm 3.2$	$176.9 \pm 20.6$	$11.4 \pm 1.3$	$68.5 \pm 5.3$
<i>Air</i>	$30.3 \pm 2.8$	$180.3 \pm 24.1$	$6.7 \pm 0.6$	$139.5 \pm 17.8$

### 6.3.2. Pollutant build-up and pollutant wash-off models

Process-based models were developed to predict airborne pollutant loads in stormwater runoff. However, as the model performed poorly, the results are discussed in Appendix A. The coefficients values derived from eq. 6-1 and eq. 6-2 did not behave as scientific theory would suggest. This was not surprising as the assumption used to derive the coefficients was intrinsically flawed. It was assumed that after a large rain event (rain depth > 20 mm; rain intensity > 5mm/h) all pollutants built-up on the pavement surface were removed by the rain

event; thus, enabling the coefficients for the build-up and wash-off equations to be obtained. This assumption was however invalid - it is known that a most storm events do not remove the total load, instead, a 'fixed' load remains adhered to the surface (Vaze and Chiew 2002). Additionally, the fixed load remaining on the pavement surface will vary for different storm events so a constant term describing the fixed load cannot be inputted into the model without appropriate model calibration (which is beyond the scope of this research). The model was calibrated with only a small data set ( $n=3$ ) that conformed to the large rain event criteria, which was insufficient for adequate model calibration. Therefore, statistical techniques were used instead to derive a stormwater quality model because the assumption of complete pollutant removal was not required.

### ***6.3.3. Regression models for predicting stormwater pollutant loads***

#### *6.3.3.1. Mixed-effect models for predicting stormwater pollutant loads*

Various models were considered using different combinations of the independent variables and their transformations. The numerical results of the 'best' models are represented in Table 6-8. Selecting the appropriate independent variables was imperative for an accurate model as many different variables can influence stormwater pollutant build-up and wash-off. Selecting the independent variables was fundamentally a trial and error process that was dependent on the creativity and subjectivity of the modeller (Irish et al. 1998). Computer-aided packages are also available which can generate a set of models with different combinations of independent variables, e.g. the "dredge" procedure in the MuMIn package (Barton 2014) for the program R (R Core Team 2014). However, these procedures should be used with caution as they may result in a spurious "best" model caused by the model selection bias (Barton 2014). Regression modelling of stormwater quality had an added complexity with highly correlated independent variables (e.g. rain depth and runoff intensity). Inclusion of highly correlated variables into a single model violates a major assumption of regression analyse rendering the model invalid. Although, multicollinearity (strong correlations) will not alter the predictive

performance of the regression model, it will conceal the effect of each independent variable on the dependent variable (Irish et al. 1998). Therefore, only non-correlated independent variables were inputted into the models.

For each land-use area, it was found that the independent variables ADD and RD explained most of the variation in Cu and Zn loads. The independent variables ADD, RI, and Dur explained most of the variation in Pb and TSS loads. In all cases, the ‘best’ model was represented by a log-arctan relationship for pollutant build-up and a log-log relationship for pollutant wash-off. Similarly, Driver and Tasker (1990) found that the logarithm transformation was typically the best transformation for the independent variables. Atmospheric pressure, relative humidity, and temperature did not have a significant effect on pollutant loadings. Wind direction and speed on occasion had a significant effect on pollutant loadings. However, as they did not add greatly to the predictive power (added 1-2%) of the models, they were excluded from the ‘best’ parsimonious models.

The ‘best’ models performed well when estimating pollutant-load trends over time in each land-use area, as exemplified by Figure 6-1. The models were moderately successful in estimating pollutant loads from the validation data (Table 6-8), which can be useful for general stormwater planning processes. The Nash Sutcliffe efficiency values for all models were greater than zero; therefore, the models were better at predicting the pollutant loads than the mean observed pollutant loads (Legates and McCabe 1999). To try to improve the model, the data was split into two categories: large and small rain events. A large rain event was categorised as having a rain depth greater than 5 mm and a small rain event was less than 5 mm (5 mm was chosen because it was the median value for rain depth). As the split models did not perform satisfactorily (poor predictive performance), the results are discussed in Appendix B. The models in this study (Table 6-8) performed better than those generated by Driver and Tasker (1990), who obtained  $R^2$  values of 0.41 for Cu, 0.46 for Pb, and 0.59 for Zn when monitoring the annual pollutant loads from an urban catchment. Additionally, the models performed better than the models generated by Kayhanian et al. (2007), who obtained  $R^2$  values of 0.52 for total Cu event mean concentrations (EMC's), 0.36 for total Pb EMC's, and 0.51 for total Zn EMC's when modelling highway runoff. However, the models in this

study performed worse than the prediction models developed by Irish et al. (1998), who obtained  $R^2$  values of 0.90 for Cu, 0.68 for Pb, and 0.92 for Zn when monitoring highway runoff. Although the derived models can predict approximately 53% to 69% of the variation in pollutant loads, there remained a large quantity of the variation unexplained. This uncertainty is a common problem shared with all models - to collect enough data to characterise pollutant loads or concentrations that occur from a full spectrum of rain events is physically impossible and cost-prohibitive (Vaze and Chiew 2003a). In addition, error occurred from the variability of stormwater data due to the random nature of the storm event, sampling, and analyses error (Jewell and Adrian 1982). For example, the percentage error in measuring Cu and Pb by ICP-MS (Agilent) was approximately 0.03% and 2.1%, respectively, at the 1  $\mu\text{g/l}$  level and approximately 1.5% for Zn at the 10  $\mu\text{g/l}$  level, which may explain some of the error in the model. Another known difficulty with modelling the data was taking a representative value for Rh, P, and T over the antecedent dry period. A median value over the entire dry period (which can range from 0 - 27 dry days) was taken to represent Rh, P, and T, which may not have been suitable. However, this is an inherent problem when monitoring pollution data from natural rainfall, whereby, the meteorology conditions cannot be controlled. In addition, the same data for Rh, P, and T (measured from a local weather station) was used for each area studied, which may have been a source of error as local variations were not taken into consideration. It is also possible that the short-term activities occurring in each land-use area influenced pollutant loads, e.g. fire training on the airside area. These activities were not represented in the model due to the complexity of monitoring them.

The results show that the model coefficients varied for each land-use area (Table 6-8). Therefore, the models presented here, like other regression models, were site-specific and were not applicable to other catchments (Haster and James 1994). Similarly, Jewell and Adrian (1982) found varying values for the estimated parameters, even among basins in the same geographic location, reinforcing the importance of gathering data from each watershed to be examined and developing independent models with this data. The results also showed that calibrating predefined models (typical for process-based models) for different pollutants are not suitable; instead, models need to be calibrated separately to suit the pollutant of concern.

**Table 6-8 Model summary of the best fitted values for total Cu, Zn, Pb, and TSS, including the error (%) between the measured and modelled ‘validation’ data (% error).**

**(a) Total Cu**

<b>Model: <math>\log_{10}(\text{Cu}) = a*[\arctan(\text{ADD})] + b*[\log_{10}(\text{RD})] + \varepsilon</math></b>						
	a	b	$\varepsilon$	$R^2$	E of cal	% error
<i>Ind</i>	0.41379	0.39346	1.06783	0.637 <sub>(R2m)</sub> 0.643 <sub>(R2c)</sub>	0.39	14.2 ± 2.9
<i>Res</i>	0.54144	0.41950	0.42101	0.642 <sub>(R2m)</sub> 0.642 <sub>(R2c)</sub>	0.40	14.3 ± 2.7
<i>Air</i>	0.25681	0.68541	0.46709	0.655 <sub>(R2m)</sub> 0.655 <sub>(R2c)</sub>	0.47	21.6 ± 3.9

**(b) Total Zn**

<b>Model: <math>\log_{10}(\text{Zn}) = a*[\arctan(\text{ADD})] + b*[\log_{10}(\text{RD})] + \varepsilon</math></b>						
	a	b	$\varepsilon$	$R^2$	E of cal	% error
<i>Ind</i>	0.30480	0.57749	1.70805	0.586 <sub>(R2m)</sub> 0.586 <sub>(R2c)</sub>	0.23	11.0 ± 1.8
<i>Res</i>	0.24443	0.78791	1.04139	0.586 <sub>(R2m)</sub> 0.586 <sub>(R2c)</sub>	0.42	13.8 ± 2.1
<i>Air</i>	0.10805	0.87161	1.18177	0.577 <sub>(R2m)</sub> 0.596 <sub>(R2c)</sub>	0.29	15.7 ± 2.6

**(c) Total Pb**

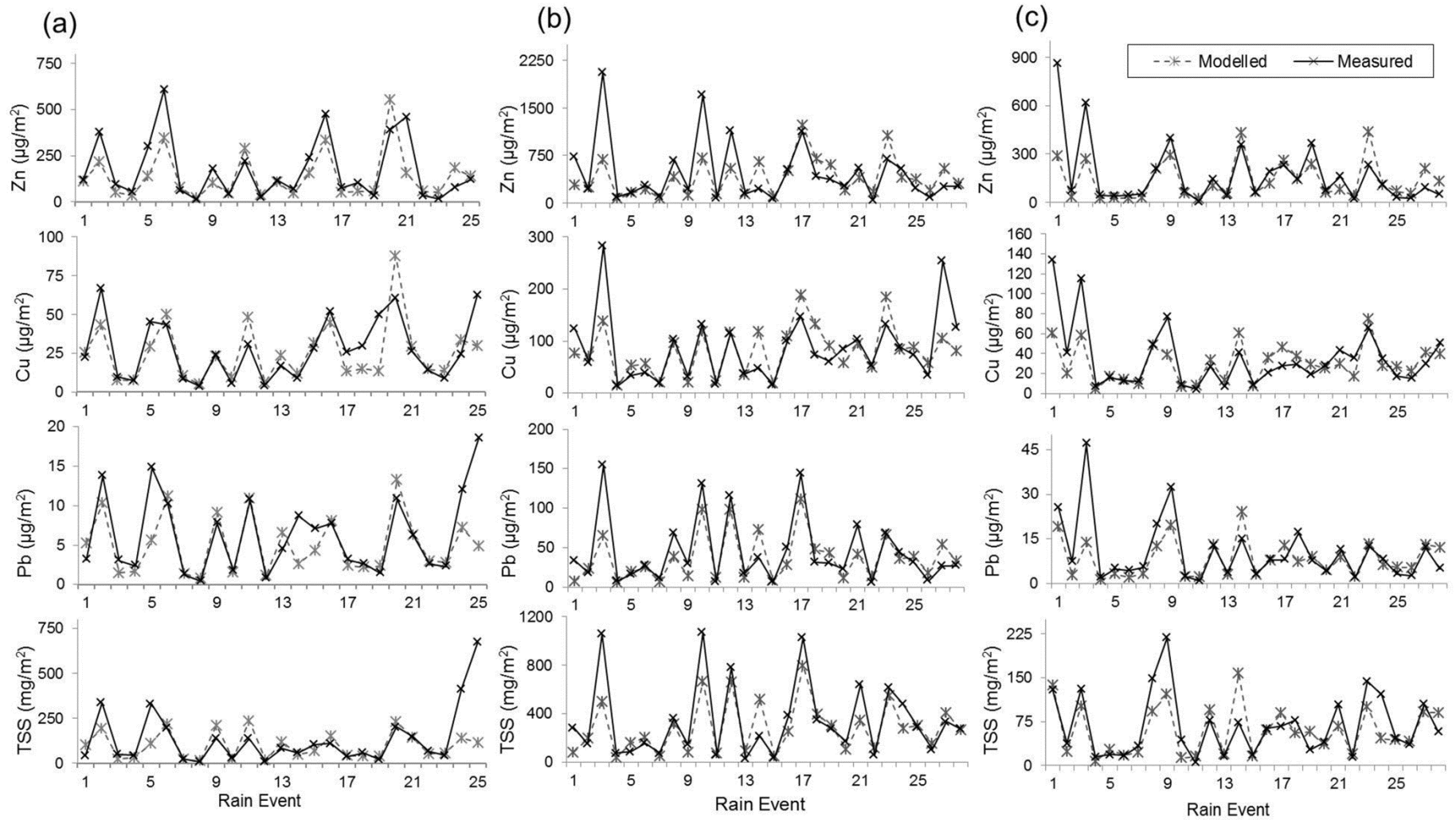
Model: $\log_{10}(\text{Pb}) = a * [\arctan(\text{ADD})] + c * [\log_{10}(\text{RI})] + d * [\log_{10}(\text{Dur})] + \varepsilon$							
	a	c	d	$\varepsilon$	R <sup>2</sup>	E of cal	% error
Ind	0.21522	0.80159	0.16608	0.91799	0.620 <sub>(R2m)</sub>	0.45	17.4 ± 4.1
					0.622 <sub>(R2c)</sub>		
Res	0.31695	0.67882	0.19753	0.08699	0.557 <sub>(R2m)</sub>	0.22	32.2 ± 2.1
					0.531 <sub>(R2c)</sub>		
Air	0.27578	0.66307	0.59686	-0.45728	0.614 <sub>(R2m)</sub>	0.11	31.4 ± 5.0
					0.625 <sub>(R2c)</sub>		

**(d) TSS**

Model: $\log_{10}(\text{TSS}) = a*[\arctan(\text{ADD})] + c*[\log_{10}(\text{RI})] + d*[\log_{10}(\text{Dur})] + \varepsilon$							
	a	c	d	$\varepsilon$	R <sup>2</sup>	E of cal	% error
<i>Ind</i>	0.31244	0.67911	0.21683	1.66858	0.630 <sub>(R2m)</sub> 0.640 <sub>(R2c)</sub>	0.40	10.6 ± 3.5
<i>Res</i>	0.41598	0.61615	0.19047	0.84877	0.634 <sub>(R2m)</sub> 0.644 <sub>(R2c)</sub>	0.35	11.7 ± 2.8
<i>Air</i>	0.32954	0.81632	0.48434	0.84432	0.686 <sub>(R2m)</sub> 0.686 <sub>(R2c)</sub>	0.43	13.2 ± 2.2

Note:  $R^2_{(m)}$  = variance explained by the fixed factors,  $R^2_{(c)}$  = variance explained by the fixed and random factors, E = Nash Sutcliffe efficiency





**Figure 6-1 Measured and modelled results (combined calibration and validation data) of atmospheric pollutant loads in stormwater runoff from (a) Air, (b) Ind, and (c) Res.**

#### **6.3.4. Influencing meteorological variables**

##### **6.3.4.1. Pollutant build-up**

ADD was found to significantly influence pollutant build-up in all land-use areas. The best fit to the observed data occurred when ADD was arctan transformed. This result was similar to the findings by Gunawardena et al. (2011) and Wicke et al. (2010). They found that pollutant build-up increased asymptotically (exponential function) with ADD, which ultimately plateaued after 6 days. However, in a ‘real’ (non-simulated) urban environment pollutant build-up may be further disturbed by other surface removal processes (e.g. streets sweeping and traffic flows) which can reduce the amount of pollutants available for wash-off (McPherson et al. 2013). No significant relationship was found between P, Rh, and T prior to rainfall and pollutant loads; therefore, these were not considered an influencing factor in pollutant build-up in this study. The influence of wind characteristics on pollutant build-up was difficult to discern in this research – in certain models, wind had a significant effect but it did not explain much of the variance in the data. This was likely due to the limitations in taking a representative value (mean and median) of WS and WD over the entire antecedent dry period. It is recommended that more research be conducted into wind characteristics and its effect on pollution build-up in stormwater studies.

##### **6.3.4.2. Pollutant wash-off**

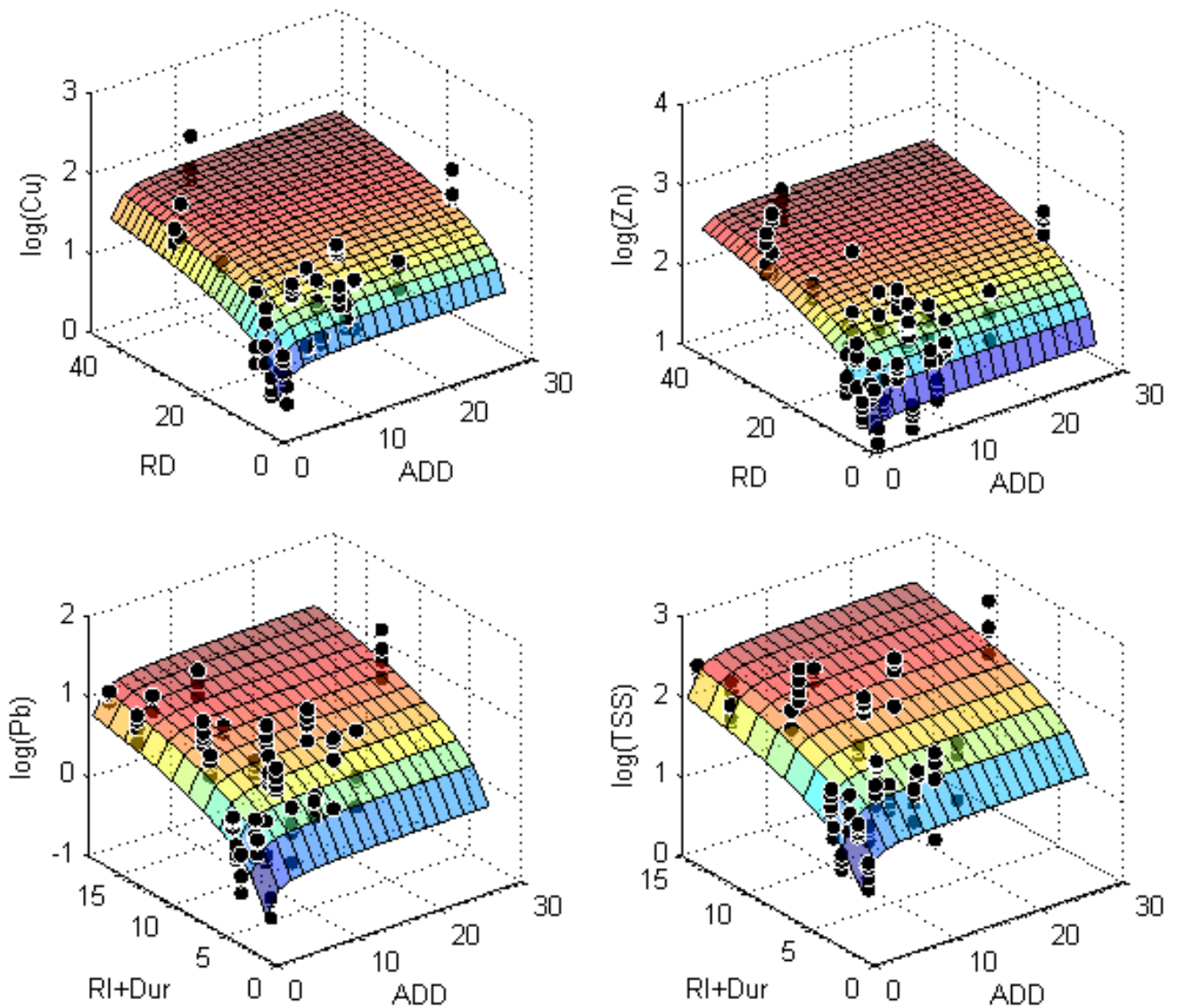
The relationship between pollutant wash-off and rainfall characteristics seemed to be contingent on the pollutant of concern. For all land-use areas, Cu and Zn showed a significant relationship with RD; total Pb and TSS displayed a significant relationship with RI and Dur. This suggested that the pollutant speciation phase plays an important role in surface wash-off. Total Pb is typically associated with the particulate phase (Wicke et al. 2012b; Prestes et al. 2006). Similarly, total Pb was principally in the particulate form as concentrations of dissolved Pb in runoff were frequently below the 1 µg/l detection limit. Therefore, as RI increased more particulates had the ability to be mobilised from an impermeable surface,

which resulted in higher loads of Pb and TSS in runoff. With 75% of available particulates removed during a 20 mm/h rain event and most of the particulates being removed during a 115 mm/h rain event (Egodawatta et al. 2009), it can be assumed that TSS and total Pb loads would be the highest during these (rare) high intensity rain events. The relationship between Pb, TSS and Dur likely resulted from a fraction of particulates being consistently removed throughout the duration of the rain event (Barrett et al. 1995). Egodawatta et al. (2007) similarly found that rainfall intensity and duration were the most suitable covariates for predicting TSS in wash-off from roof and road surfaces using process-based models. Both RI and Dur had a significant effect on pollutant loads when they were log-transformed; this suggested, that at the start of a rain event the rate of pollutant wash-off was at its greatest, but this slows as the duration and intensity of the rain event increased. Conversely, RD had a greater influence on pollutants that have a high portion in the dissolved phase (see Table 6-9). Thus, as RD increased more pollutants will desorb from the impermeable surface; thus, increasing the pollutant loads in runoff. In all cases, RD had the strongest relationship with pollutant loads when it was log-transformed. This suggested that the majority of pollutants were washed-off at the start of a rain event but the rate of pollutant wash-off declined as the rain event continued.

Figure 6-2 exemplifies how pollutant loads in stormwater runoff changes when pollutant build-up and wash-off increases based on the model outputs for the Air land-use area. Air was taken as a representative of the other land-use areas. In general, pollutant wash-off had the greatest influence on pollutant loads in runoff while pollutant build-up had only a minor influence (primarily with ADD). Vaze et al. (2003b) found that pollutant build-up was always higher than what could be washed-off. Therefore, pollutant wash-off was the transport-limiting factor, which perhaps explains why it had more of an influence over pollutant loads in runoff from impermeable surfaces.

**Table 6-9 Percentage contribution (mean  $\pm$  S.E.) of dissolved Cu and Zn to their total loadings. Dissolved Pb was not included as it was frequently below the detection limit.**

	Dissolved Cu to total Cu (%)	Dissolved Zn to total Zn (%)
<i>Ind</i>	$31.2 \pm 2.3$	$32.2 \pm 2.4$
<i>Res</i>	$47.1 \pm 2.4$	$51.0 \pm 2.2$
<i>Air</i>	$46.6 \pm 2.5$	$50.1 \pm 2.8$



**Figure 6-2 Estimated changes in pollutant loads based on the models generated versus measured pollutant loads.**

## 6.4. Conclusions

This monitoring campaign enabled the relationships between rainfall characteristics and individual pollutant behaviours to be investigated over different land-use areas. Mixed-effect models were found to be an effective tool for determining the variables influencing pollutant-specific build-up and wash-off dynamics. Antecedent dry days were found to exert a significant influence on Cu, Zn, Pb, and TSS loads in stormwater runoff. Rainfall intensity, rainfall duration and rainfall depth also had a significant influence, although this was dependent on the speciation phase of the pollutant. Particulate pollutants, i.e. Pb and TSS, were controlled by rainfall intensity as more particulates have the potential to be mobilised from a surface when the energy imparted by the falling raindrops increased. Rain depth influences pollutants that had a high proportion in their dissolved phase because more pollutants had the ability to desorb from a surface.

The models presented were site-specific and were not applicable to other catchments; however, the techniques described here could be used as a relatively quick and effective tool for creating customised models for estimating pollutant loads for different pollutants and catchments. Customising models with local data to suit the pollutant (and catchment) of concern will improve the precision of stormwater quality models and will lead to a better comprehension of local stormwater quality. Like other stormwater quality models, the models described here had difficulties in accurately predicting stormwater quality because of inherent variability of stormwater data. However, the models were useful in predicting pollutant trends over time.

# Chapter Seven:

## The Contribution of Particulate Matter and Wet Deposition to Total Copper, Lead, and Zinc Deposition

## **7. THE CONTRIBUTION OF PARTICULATE MATTER AND WET DEPOSITION TO TOTAL COPPER, LEAD, AND ZINC DEPOSITION**

### **7.1. Introduction**

#### ***7.1.1. Particulate matter***

Particulate matter (PM) is an atmospheric pollutant that is defined by its size rather than its chemical nature, structure, or origin (Grantz et al. 2003). PM is not a single pollutant, but rather a heterogeneous composite of particles varying in chemical composition, shape, size, solubility, residence time, toxicity, and origin (Grantz et al. 2003; Tecer et al. 2008). PM is typically subdivided into two categories: PM<sub>2.5</sub> and PM<sub>10</sub>. PM<sub>2.5</sub> composes of particles with a diameter smaller than 2.5 µm and are referred to as “fine” particles. PM<sub>10</sub> refers to particles with a diameter smaller than 10 µm, which also encompasses the PM<sub>2.5</sub> fraction. Particles with a size range between 2.5 µm and 10 µm are called “coarse” particles. In most urban environments, both coarse and fine particles are present together, but the proportion of fine to coarse particles varies between different urban airsheds depending on the local geography, meteorology, and the emission source(s) (WHO 2006). Fine particles, in comparison to coarse particles, have longer atmospheric residence time and can be carried long distances, in some instances travelling 1,000 - 10,000 km from their source (Grantz et al. 2003).

PM concentrations are altered by atmospheric relative humidity, rainfall, atmospheric stability, and pollutant dispersal (Grantz et al. 2003; Tecer et al. 2008), as discussed in Table 7-1. In addition, PM undergoes various physical and chemical transformations in the atmosphere, i.e. changes to particle structure, size, and composition from processes, such as, coagulation, gas uptake, restructuring, chemical reactions (Mukhtar and Limbeck 2013). Thus, the concentration and composition of PM are highly variable even within the same airshed.

**Table 7-1 Variables influencing PM concentrations.**

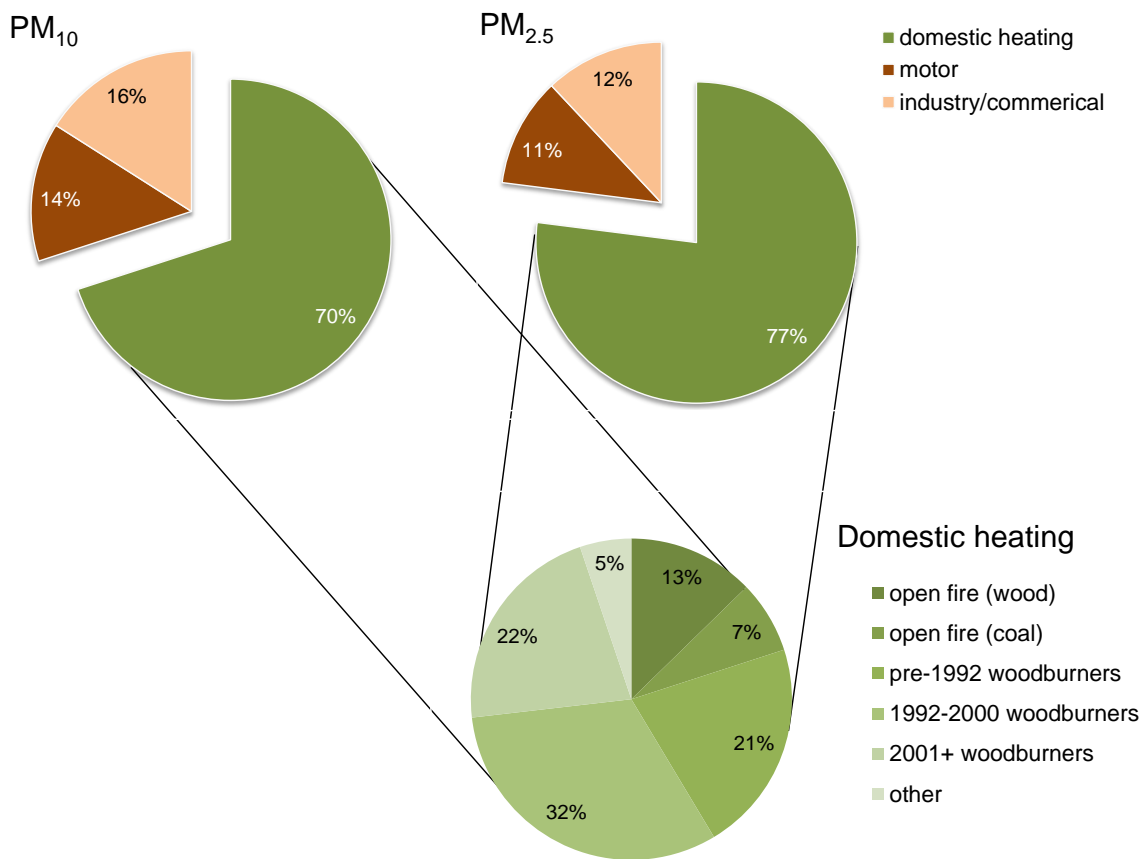
<b>Variable</b>	<b>Description</b>
<i>Atmospheric humidity</i>	Increases the concentration of PM <sub>10</sub> via particle growth mechanisms, e.g. hygroscopic growth and condensation of particles (Lee and Park 2010).
<i>Rainfall</i>	Decreases PM <sub>10</sub> and PM <sub>2.5</sub> concentrations through atmospheric wash-out processes (Tecer et al. 2008).
<i>Atmospheric stability</i>	Increases PM <sub>10</sub> concentrations as lower wind speeds reduce the dispersion of heavy particulates; conversely, PM <sub>2.5</sub> concentrations are less affected by atmospheric stability (Lee and Park 2010).
<i>Wind direction</i>	Affects PM concentrations by altering their dispersal patterns.

Christchurch, New Zealand, is known to have a serious PM<sub>2.5</sub> and PM<sub>10</sub> wintertime pollution problem (CCC 2011; Spronken-Smith et al. 2002). The major source of PM<sub>2.5</sub>, and thus PM<sub>10</sub>, is home heating emissions (CCC 2006), as exemplified in Figure 7-1. Thus, to reduce PM concentrations, a ban on solid-fuel open fires usage from 1 April to 30 September each year was introduced by the Ministry for the Environment – Regulation 24A (MfE 2011b) in 2010. In New Zealand, PM<sub>10</sub> pollution is regulated by the National Environmental Standard for Air Quality (NES). The NES requires that no airshed should have PM<sub>10</sub> concentrations exceeding 50 µg/m<sup>3</sup> more than once per year by 2020 (MfE 2011a). Currently there are no regulations controlling ambient PM<sub>2.5</sub> concentrations; instead monitoring standards based on the World Health Organisation (WHO 2006) guideline values (25 µg/m<sup>3</sup> for the 24-hour average and 10 µg/m<sup>3</sup> for the annual average) are employed (Salomon 2014).

The majority of regulation and research initiatives involving PM are driven by its effects on human health (Grantz et al. 2003), unsurprisingly, as the WHO considers PM as a major risk factor for human health (WHO 2006). In particular, fine particles (PM<sub>2.5</sub>) are associated with the most adverse health effects from particulate air pollution because they can penetrate and lodge deeply in the lungs (WHO 2006). For example, Amann et al. (2005) found that elevated PM<sub>2.5</sub> concentrations reduce the life expectancy of Europeans by 5 - 6 months. Additionally, PM can also be a substantial source of organic and inorganic pollutants. For example, fine particles are typically composed of SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, organic carbon, elemental carbon, and heavy metals; coarse particles (PM<sub>10-2.5</sub>) are typically composed of bioaerosols (e.g. pollen),



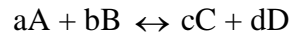
geological material, sea salt spray (Salomon 2014). PM containing heavy metals are important to research because they can exist in varying chemical forms, i.e. water soluble, loosely particulate bound, or inaccessible forms (Awan et al. 2013), and can be incorporated into stormwater pollution. In general, heavy metals are associated with fine particulates because fines have a greater surface area per unit mass, which accumulates metals more efficiently (Li et al. 2013). As fine particulates have a longer residence time in the atmosphere, concentrations typically are more homogeneously distributed in an airshed as they get farther from the emission source (Watson and Chow (2013) cited in Salomon (2014)). The main removal process of PM metals from the atmosphere is via wet deposition (Grantz et al. 2003).



**Figure 7-1 Emissions sources of PM<sub>10</sub> and PM<sub>2.5</sub>, including a breakdown of emissions from home heating appliances contributing to PM<sub>10</sub> and PM<sub>2.5</sub> concentrations. Data based on a typical winter (Jun-Aug) weekday in Christchurch City in 2009 (Smithson 2011).**

### 7.1.2. Wet deposition

Wet deposition, as described in Section 2.2 of this Thesis, is the leaching of particles from the atmosphere with water droplets in the form of rain, snow, fog, mist, dew, and frost (Göbel et al. 2007). Wet deposition is one of the most important mechanisms through which airborne pollutants reach the land surface (Polkowska et al. 2011). Wet deposition removes approximately 70-80% of the pollutants, principally PM<sub>2.5</sub>, from the atmosphere (Lindberg and Harriss 1981; Radke et al. 1980). However, this amount is dependent on the airshed studied, the chemical species, and the frequency of precipitation events (Poissant et al. 1994). Aside from being a major atmospheric pollutant removal pathway, wet deposition is important because it leaches pollutants to a surface partly in solution, enhancing the possibility of biological interactions (Lindberg 1982). The solubility of the pollutant is affected by rainfall pH, pollutant concentration (see eq7-1), and the type of particle the pollutant is affiliated with in the atmosphere (Kaya and Tuncel 1997). Determining the ability of a metal to dissolve in rain is governed by equations 7-1, 7-2, & 7-3. A metal will be soluble in rain when SI < 1; when SI > 1, the metal will be in the particulate form; when SI = 1 the metal and precipitation solution is at equilibrium.



$$k = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad \text{eq. 7-1}$$

$$IAP = [A]^a [B]^b \quad \text{eq. 7-2}$$

$$SI = IAP/k \quad \text{eq. 7-3}$$

Where: k = solubility product; [ ] denotes concentration; aA and bB are the reactants; cC and dD are the products; IAP = ion activity product; SI = saturation index.

Wet deposition is related to precipitation amount, meteorology, topography, pollutant solubility, and the pollutant atmospheric concentration (Grantz et al. 2003; Polkowska et al. 2011). Wet deposition becomes runoff after contact with the land surface (Polkowska et al. 2011). The runoff incorporates dry-deposition particles, which results in bulk deposition loads from an impermeable surface. As the frequency of rainfall is low for Christchurch (approximately 81 rain days per year), it is assumed that wet deposition will not influence the bulk deposition loads as much as dry deposition. However, it is important to quantify the contribution of both wet and dry deposition to bulk deposition loads for accurate knowledge on local atmospheric deposition processes. This research quantified the contribution of wet deposition to the total Cu, Zn, and Pb deposition flux in the Christchurch airshed. In addition, ambient PM concentrations were assessed for relationships with wet deposition loads for Cu, Zn, and Pb.

## **7.2. Materials and Methods Overview**

Wet deposition samples were quantified for Cu, Pb, and Zn from August (winter) 2013 to March (autumn) 2014. Ambient PM concentrations were also quantified ( $PM_{2.5}$ ,  $PM_{10}$ , and  $PM_{10-2.5}$ ). PM data (24-hour averages) were obtained from the Environment Canterbury (ECan) air-monitoring station in Woolston, Christchurch (industrial land-use area). A wet deposition sampler (N-Con ADS Model 00-120-2) was deployed adjacent to the ECan particulate matter sampler. Results from the wet deposition samples were directly compared to bulk deposition ( $BD_{con}$ ) runoff loads from the ‘concrete board’ experimental setup deployed in the Ind research site (1.44 km away). Rainfall data was obtained from Christchurch City Council’s weather station located 0.87 km away.

### 7.3. Results and Discussion

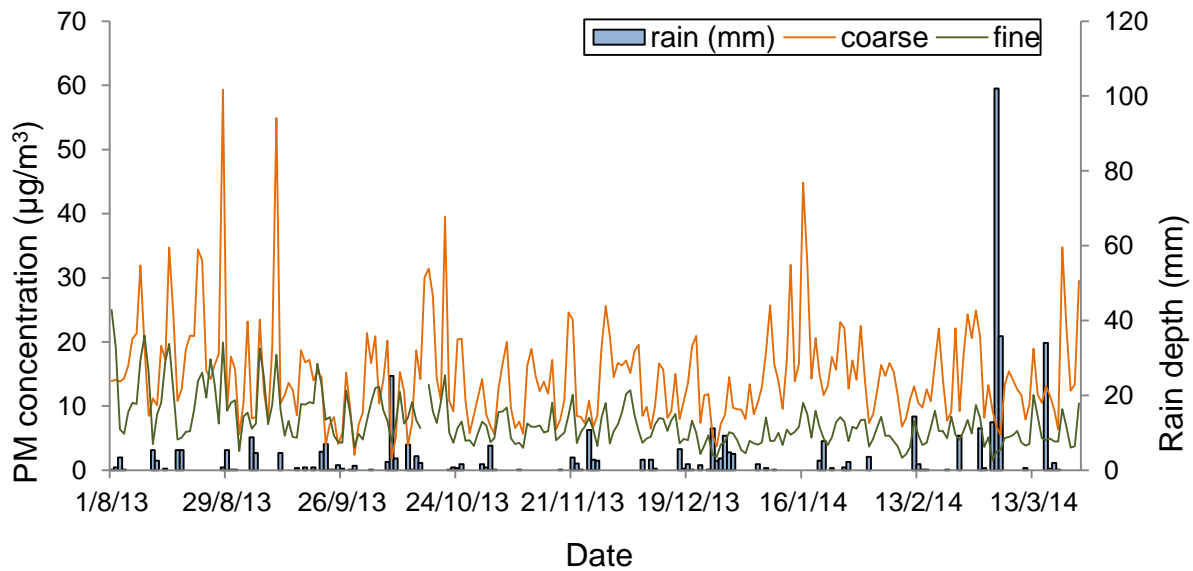
#### 7.3.1. *Data summary*

Seventeen rain events were sampled to analyse the interaction between wet deposition (WD) loads and PM (Table 7-2). Figure 7-2 exemplifies the fine ( $PM_{2.5}$ ) and coarse ( $PM_{10-2.5}$ ) particulate concentrations over the sampling period. Eight wet deposition samples were measured that could be directly compared to pollutant loads from Con runoff ( $BD_{con}$ ) (Table 7-2). A summary of wet deposition pollutant loads and  $PM_{2.5}$ ,  $PM_{10}$ , and  $PM_{10-2.5}$  concentrations are shown in Table 7-3. PM concentrations the day preceding the rain event and the average PM concentrations over the antecedent dry period were analysed. At the industrial air-monitoring site, the coarse fraction dominated particulate matter concentrations; therefore, the particulate matter was principally from geological matter, sea salt spray, and/or bioaerosols (Salomon 2014). A summary of total Cu, Pb, and Zn loads from WD and  $BD_{con}$  are exemplified in Table 7-4.

Graphs displaying daily  $PM_{10}$  and  $PM_{2.5}$  concentrations over the antecedent dry period versus total Cu only (taken as a representative of the other pollutants) concentrations in WD and  $BD_{con}$  are discussed in Appendix C.

**Table 7-2 Summary of rain events captured during the sampling campaign.**

Measured	Rain event	Date	RD (mm)	ADD (d)
WD & BD	1	03/08/13	5.8	10
WD & BD	2	25/09/13	2.0	2.7
WD & BD	3	08/10/13	33	8
WD & BD	4	13/10/13	8.4	2.5
WD & BD	5	25/10/13	5.6	7
WD & BD	6	31/10/13	2.0	5.5
WD	7	22/11/13	5.6	19.6
WD & BD	8	25/11/13	13.0	3
WD & BD	9	08/12/13	3.8	11
WD	10	17/12/13	5.2	6.8
WD	11	20/01/14	10.6	13.5
WD	12	26/01/14	3.6	5.4
WD	13	12/02/14	15.6	11.2
WD	14	23/02/14	9.6	9.4
WD	15	28/02/14	11.8	4.8
WD	16	03/03/14	138.4	2.1
WD	17	05/03/14	1.8	0



**Figure 7-2 Fine and coarse particulate matter concentrations over the sampling period and rainfall depth.**

**Table 7-3 The range (min – max) and mean values of particulate matter a day prior to the rain event (before rain), averaged PM concentrations over the antecedent dry period (average), and total metals in wet deposition.**

	Before rain ( $\mu\text{g}/\text{m}^3$ )			Average ( $\mu\text{g}/\text{m}^3$ )			$\text{tCu}_{(\text{WD})}$	$\text{tZn}_{(\text{WD})}$	$\text{tPb}_{(\text{WD})}$
	$\text{PM}_{10}$	$\text{PM}_{2.5}$	$\text{PM}_{10-2.5}$	$\text{PM}_{10}$	$\text{PM}_{2.5}$	$\text{PM}_{10-2.5}$	( $\mu\text{g}/\text{m}^2$ )	( $\mu\text{g}/\text{m}^2$ )	( $\mu\text{g}/\text{m}^2$ )
<i>Range</i>	8.6 – 185.7	3.1 – 48.2	5.5 – 24.9	8.6 – 107.4	3.1 – 36.8	5.5 – 23.5	1.5 – 509.2	17.4 – 888.6	0.3 – 130.3
<i>Mean <math>\pm</math> SE</i>	31.9 $\pm$ 9.5	10.2 $\pm$ 2.6	15.1 $\pm$ 1.4	26.3 $\pm$ 5.5	8.7 $\pm$ 1.9	14.0 $\pm$ 1.3	56.5 $\pm$ 28.3	213.6 $\pm$ 56.7	20.2 $\pm$ 9.0

**Table 7-4 The range (min – max) and mean values of total metals ( $\mu\text{g}/\text{m}^2$ ) in bulk deposition from August 2013 to December 2013 and the ratio of pollutant in wet deposition to bulk deposition (%). Where “n/d” = not detected and “-” represents results not analysed due to insufficient data.**

	dCu	tCu	dZn	tZn	dPb	tPb
<i>Min</i>	15.7	34.7	26.4	36.4	n/d	3.4
<i>Max</i>	202.9	254.3	223.1	693.7	0.9	78.5
<i>Mean <math>\pm</math> SE</i>	62.8 $\pm$ 20.0	108.3 $\pm$ 22.4	118.1 $\pm$ 26.4	334.2 $\pm$ 77.6	-	35.8 $\pm$ 8.8
<i>Ratio (%) to WD (mean <math>\pm</math> SE)</i>	12.4 $\pm$ 6.4	10.4 $\pm$ 2.5	132.7 $\pm$ 11.2	34.2 $\pm$ 5.3	-	11.6 $\pm$ 3.4

### 7.3.2. Particulate matter with varying antecedent dry periods

A MANOVA statistical analysis was conducted to ascertain if there was a significant difference in fine and coarse particulate concentrations with varying antecedent dry periods. The antecedent dry periods were categorised into six groups: 0-<1 d, 1 - <2.5 d, 2.5 – <4 d, 4 – <5.5 d, 5.5 – 7 d, >7 d. The mean concentrations of ambient fine ( $\text{PM}_{2.5}$ ) and coarse ( $\text{PM}_{10-2.5}$ ) particles varied significantly with changing antecedent dry periods (Pillai's trace [ $V = 0.17$ ,  $F(10, 454) = 4.11$ ,  $p\text{-value} < 0.01$ ]). For coarse particles, there was a significant difference in their concentrations when the antecedent dry period was between 0-1 d. After one antecedent dry day, the concentrations of coarse particles did not alter significantly with increasing antecedent dry days (Table 7-5). Similarly, for fine particles, there was a significant difference in their concentrations when the antecedent dry period was between 0-

2.5 d. After 2.5 antecedent dry days, the concentrations of fine particles did not alter significantly with increasing antecedent dry days (Table 7-5). Therefore, wash-off from a precipitation event had a significant effect on fine and coarse particle concentrations within the initial few days of the rain event occurring, but both fine and coarse particle concentrations were not influenced by longer antecedent dry periods (1 to 2.5 days). This differs to particulate build-up on urban impermeable surfaces, whereby, particulate build-up increases asymptotically with antecedent dry days, which ultimately plateaus after 6 days (Section 6.3.4.1). Therefore, particulate build-up on an impermeable surface is limited at the start of the antecedent dry period by reduced concentrations of PM in the atmosphere.

**Table 7-5 The average concentrations of coarse and fine PM ( $\mu\text{g}/\text{m}^3$ ) with varying antecedent dry periods. Within each antecedent dry period, those sharing a common letter are not significantly different ( $p > 0.05$ ). Where “n” = number of cases analysed.**

	<1 d	1 - <2.5 d	2.5 - <4 d	4 - <5.5 d	5.5 - <7 d	>7 d
<i>Coarse</i>	$9.0 \pm 0.7^a$	$13.3 \pm 0.8^b$	$16.1 \pm 1.2^b$	$17.1 \pm 1.6^b$	$15.4 \pm 1.5^b$	$16.3 \pm 1.2^b$
<i>Fine</i>	$5.2 \pm 0.3^a$	$6.8 \pm 0.5^{a,b}$	$7.7 \pm 0.5^b$	$7.7 \pm 0.6^b$	$8.7 \pm 0.9^b$	$7.8 \pm 0.5^b$
<i>n</i>	30	47	43	32	27	54

### 7.3.3. *Particulate matter and wet deposition*

The relationship between fine and coarse particulate matter concentrations and heavy metal loads in wet deposition is shown in Table 7-6. Particulate matter concentrations did not show a significant relationship with heavy metal loads in wet deposition, except for Pb, which had a significant relationship with coarse particle ( $\text{PM}_{10-2.5}$ ) concentrations prior to rainfall. Therefore, coarse particle concentrations influenced Pb loads in wet deposition, which likely resulted from a local pollutant source emitting coarse Pb particulates that became easily washed-out of the atmosphere by a rain event due to their preference for the particulate phase. This finding was different to other research, which stated that Pb loads in wet deposition were mainly associated with the submicron size range (Beilke et al. 1983). However, Lee and Park (2010) also found that Cu did not correlate with PM, while Pb was highly correlated ( $p\text{-value} < 0.05$ ) to PM in air emission from an urban-residential and industrial land-use area in Ulsan,

Korea. The reason that Cu and Zn were not statistically related to PM was likely due to height of the PM monitoring setup above ground; PM concentrations were measured approximately 3 m above the ground, which only reflects PM concentrations at the lower tropospheric level. PM concentrations higher in the troposphere, e.g. where cloud formation occurs and rain-particle impaction occurs, were not represented. It was likely that the correlation between PM and Pb was due to a local source of Pb contributing to wet deposition loads, for example, from old residential houses with Pb-based paint being demolished after the Canterbury earthquakes and from adjacent roadwork's. As the source was local, it would explain why there was PM Pb concentrations in the lower troposphere – particulate Pb did not have sufficient time to reach higher altitudes in the troposphere before being washed-out.

**Table 7-6 Pearson's correlation between PM and metals (loads) in wet deposition.**

	Before rain		Average over dry period	
	PM <sub>2.5</sub>	PM <sub>10-2.5</sub>	PM <sub>2.5</sub>	PM <sub>10-2.5</sub>
<i>Total Cu</i>	0.028	0.343	-0.166	0.242
<i>Total Zn</i>	0.226	0.258	-0.077	0.216
<i>Total Pb</i>	0.153	0.642**	-0.068	0.548*

\*p-value < 0.05; \*\*p-value < 0.01

#### **7.3.4. Wet deposition**

Determining the speciation phase of metals in wet deposition is important because metals can occur in either the particulate or the dissolved phase. The partitioning of trace metals depends on the quantity and solubility of trace metals in a rain event (Conko et al. 2004). The percentage contribution of dissolved to total metals in WD (n=17) was 40.6% ± 7.4% and 83.1% ± 4.7% for Cu, and Zn, respectively. A ratio of dissolved to total Pb was not evaluated as dissolved Pb concentrations were frequently below the detection limit (1 µg/l); therefore, particulate Pb dominated the total Pb flux because Pb had a low solubility in rainwater and was principally washed-out in their particulate form. The ratio of dissolved to total Cu was relatively high, which suggested that Cu was soluble in rainwater. Zn was mainly associated with the dissolved phase (83.1%); therefore, Zn was highly soluble in rainwater. Similarly,

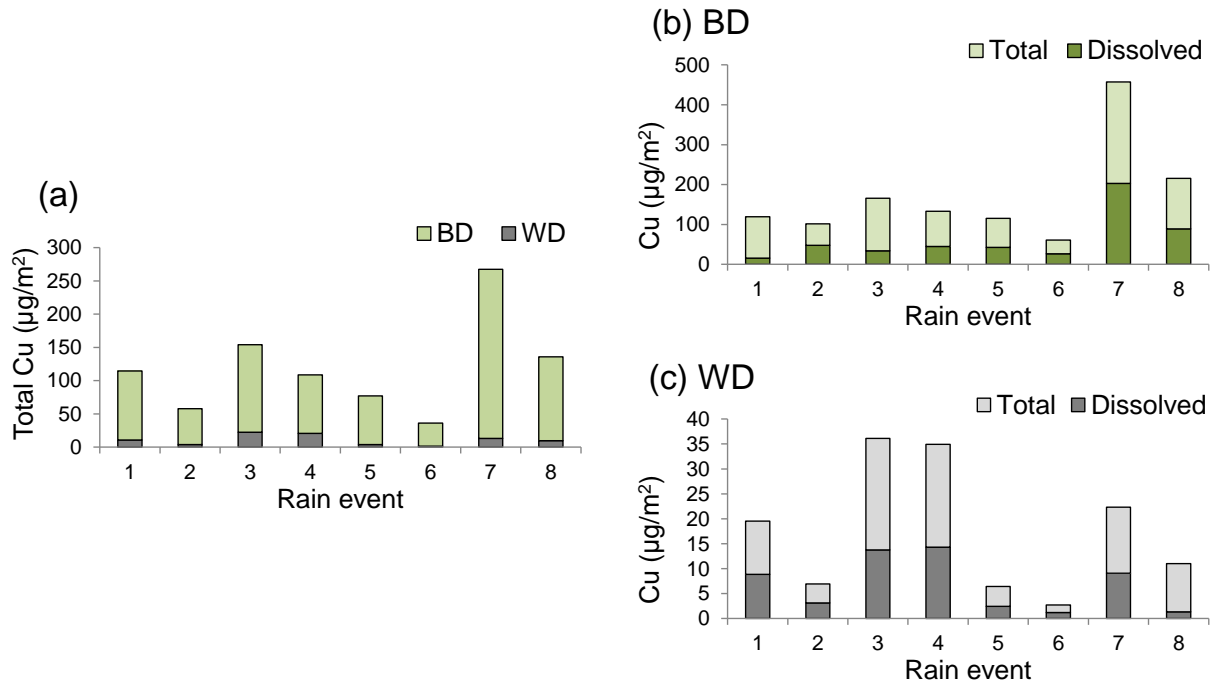


Morselli et al. (2003) found that Zn had the highest solubility in WD followed by Cu; Pb had a very low solubility in WD. Colin et al. (1990) found that Zn concentrations in wet deposition in France were mainly associated with the dissolved phase (approximately 96%). Freydier et al. (1998) found that Zn had the highest dissolved to total distribution of all metals studied (which included Pb, but not Cu) in intertropical Africa. Wet deposition results from Otago, New Zealand, found atmospheric Zn loads were present in a dissolved or easily dissolved form, and thus, stated that Zn originated from a non-crustal source because metals generated from anthropogenic sources tend to be loosely bound to airborne particles (Halstead et al. 2000). The results in this research differed to Conko et al. (2004), which found that Cu was more soluble than Zn in precipitate in Virginia, United States. However, this could be due to the lower rainfall pH in Virginia (3.7 – 4.7) than Christchurch (4.9 – 7.2) (Conko et al. 2004; Wicke et al. 2014) or from different source emissions of metals in each airshed. Kaya and Tuncel (1997) reported solubility's of  $43\% \pm 29\%$ ,  $49\% \pm 27\%$ ,  $40\% \pm 35\%$  for Zn, Cu, and Pb, respectively, in rainwater from Ankara, Turkey.

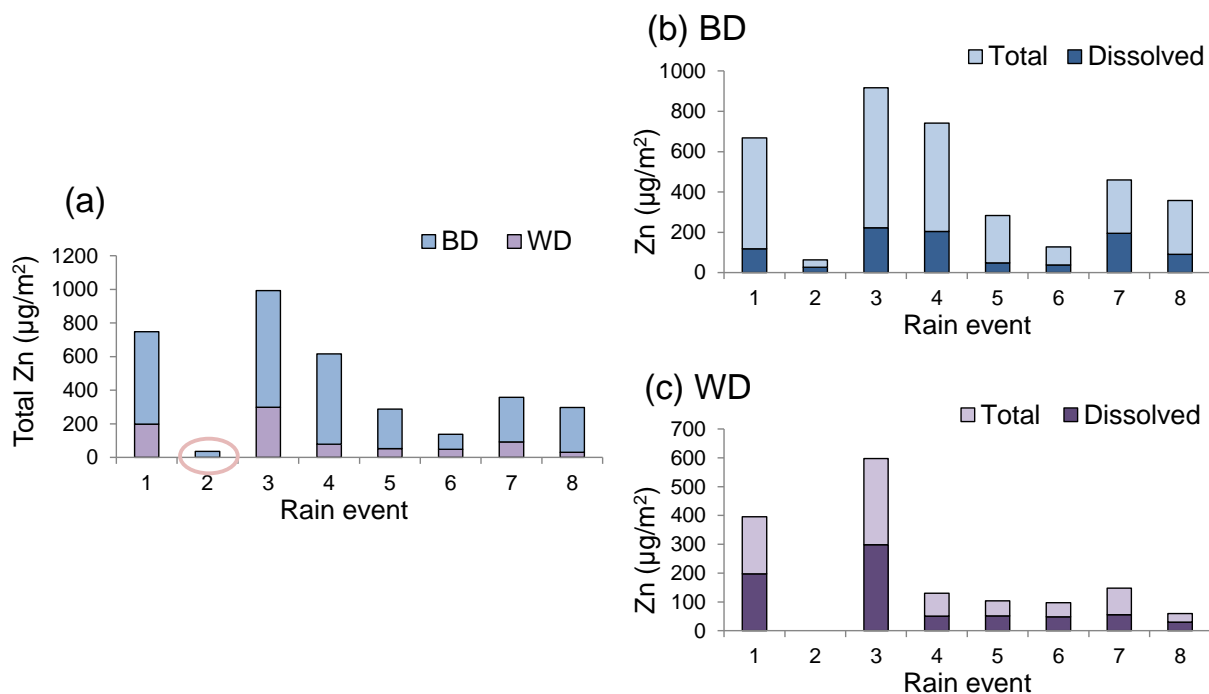
### **7.3.5. Contribution of WD to BD loads**

A summary of total Cu, Pb, and Zn loads from WD and BD<sub>con</sub> from concrete boards are exemplified in Table 7-4 (representative of the Ind site only). The results showed that wet deposition contributed approximately 10 - 13% of the total Cu, dissolved Cu, and total Pb (dissolved lead was negligible) loads in BD<sub>con</sub> (Figure 7-3 and Figure 7-5). Therefore, dry deposition was the major pathway for Cu and Pb removal from the atmosphere. Conversely, WD was an important contributor of total Zn (34%) and dissolved Zn (133%) to BD<sub>con</sub> (Figure 7-4). This was attributed to Zn being highly dissolvable in precipitate. Moreover, concentrations of dissolved Zn from wet deposition were higher than dissolved Zn concentrations in runoff from a concrete surface. The decrease in dissolved Zn in the runoff was due to calcium carbonates in the concrete immobilising dissolved Zn via calcium and Zn ion exchange (as discussed in Section 4.1.1). Although, dissolved Zn loads were dominated by WD, dry deposition was the biggest contributor to total Zn loads. The results represented here complement a study by Lindberg and Harriss (1981), which found that WD dominated

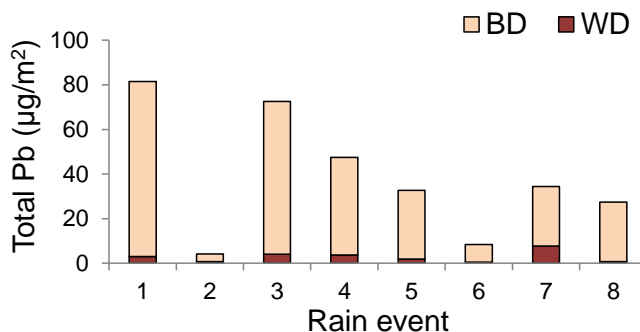
the Zn flux, whereas the Pb flux was dominated by dry deposition (Cu was not studied) in a forested canopy in Tennessee, U.S.. Overall, the results discussed here demonstrate that dry deposition was the important controller of atmospheric pollutant loads in BD<sub>con</sub>. This is due to limited precipitation in Christchurch; although dry deposition is a slow process, it is continually occurring unlike WD; therefore, it is of greater importance to net pollutant deposition. Mitigating atmospheric pollutant loads in dry deposition should be the focus of stormwater management through improved source control legislation or by choosing the best pavement material for attenuating dry deposition pollutant loads (i.e. concrete).



**Figure 7-3 (a) the quantity of total Cu in BD and WD; (b) the contribution of total and dissolved Cu in BD; and (c) the contribution of total and dissolved Cu in WD.**



**Figure 7-4 (a) the quantity of total Zn in BD and WD; (b) the contribution of total and dissolved Zn in BD; and (c) the contribution of total and dissolved Zn in WD. Zn loads in WD from rain event 2 (circled) is not represented it was below detection limit.**



**Figure 7-5 The quantity of total Pb in BD and WD. Dissolved Pb was not represented as it was frequently below detection limits.**

## 7.4. Conclusion

Knowledge of the pathways dominating atmospheric deposition is important to quantify because it increases our understanding of atmospheric pollutant removal processes. As the processes affecting pollutant deposition can vary for different airsheds due to different meteorology and land-use activities, it is important to quantify the contribution of wet and dry deposition for each airshed individually. The results presented here demonstrate the importance of WD in removing fines and coarse PM from the atmosphere. Following the rain event, atmospheric PM concentrations begin to increase; after one to two antecedent dry days, PM concentrations stabilise (i.e. PM concentrations are not influenced by longer antecedent dry periods).

While, WD removes PM from the lower troposphere, the concentrations of PM did not correlate well to Cu and Zn loads in wet deposition. This was due to the PM measurements only representing PM concentrations in the lower troposphere; PM at higher altitudes, where cloud formation occurs, was not represented. However, coarse particulate concentrations were correlated to Pb loads in WD. This suggests that there was a local source of Pb near the research site. Dry deposition was the dominant pathway for atmospheric metal removal. This was attributed to the low rainfall frequency in Christchurch. The solubility of heavy metals in precipitate was dependent on the metal of concern. Unlike Cu and Pb, Zn was highly soluble in precipitate, which resulted in the majority of Zn in WD to be associated with the dissolved phase. Therefore, WD was an important source of dissolved Zn to urban runoff.

From a stormwater manager's perspective, to manage atmospheric deposition as a source of stormwater pollution, emphasis should be placed on removing pollutant loads from dry deposition through more frequent street vacuuming practices during dry days. However, as this is not always feasible, it is recommended that more emphasis be placed on treating stormwater runoff.

# Chapter Eight: Conclusions and Recommendations

## **8. CONCLUSIONS AND RECOMMENDATIONS**

### **8.1. Conclusions**

Atmospheric deposition is known to be an important indirect source of pollutants to stormwater runoff. However, it is rarely considered by stormwater managers when implementing stormwater abatement strategies. This is principally due to the uncertainty and challenges associated with measuring and managing these contributions. This uncertainty was amplified by the dearth of knowledge on the major controllers influencing the contribution of atmospheric deposition to stormwater pollution. This research has contributed to the greater understanding of atmospherically derived pollutant build-up and wash-off dynamics. Thus, recommendations on managing atmospheric deposition as a source of stormwater pollution can be derived.

Modelling atmospheric pollutant loads in runoff is important for optimising mitigation and management measures for waterway protection. Mixed-effect regression models, as discussed in this Thesis, are a quick and effective method for predicting atmospheric pollutant loads in stormwater runoff from different catchments. Additionally, mixed-effect models are an effective tool for determining the meteorological variables that influence pollutant build-up and wash-off dynamics. Utilising regression models to estimate atmospheric pollutant loads will improve the precision of stormwater quality models and will lead to a better comprehension of local stormwater quality. This knowledge is required to help select appropriate stormwater treatment infrastructure and to determine the effectiveness of existing stormwater management strategies.

When implementing stormwater abatement strategies it is important to target the areas where most pollution occurs. This research focused on three different land-use areas to determine which areas received the greatest quantity of atmospheric pollutants. Results suggested that land-use activity was not an important factor governing atmospheric pollutant deposition loads. Instead, the orographical features of the land were more important, i.e. deposition is promoted on the windward side of a slope. Therefore, managing atmospherically derived

pollutants on windward side slopes should be of greater importance. This research found that the industrial land-use area had higher deposition rates because it was located on a base of a hill (Port Hills). Therefore, greater emphasis should be placed on treating stormwater from this location. In addition, as the industrial area will have other major sources of pollutants to stormwater (e.g., greater truck movements), focusing stormwater management on this location will provide greater water quality benefits to the nearby urban waterway.

In semi-arid environments, dry deposition is the greatest contributor to atmospheric pollutant loads. Thus, mitigating atmospheric pollutant loads before it rains via increased street vacuuming practices (using modern vacuum cleaners capable of removing PM<sub>10</sub>) will reduce the contribution of atmospheric pollution loads to stormwater. Atmospheric pollutant build-up occurs rapidly at the start of the antecedent dry period, which finally plateaus after 7-9 days; therefore, it would be more advantageous for street vacuuming to occur after seven antecedent dry days (and just prior to a rain event) when pollutant loads are at the greatest. However, due to the high cost of frequent street vacuuming, this management practice may not be feasible. Instead treating the stormwater runoff, by utilising rain gardens and engineered wetlands for example, may be more cost-effective.

Alternatively, the type of pavement used can reduce the quantities of atmospheric pollutants (and other pollutants) that are washed-off. This research discussed the benefits of utilising concrete (especially permeable concrete) in the pavement design for greater Cu and Zn retention through chemical adsorption processes. Additionally, increasing pavement roughness will also promote greater particulate pollution attenuation as more particulates are trapped within the pavements cavities. Permeable pavements are effective at removing particulate pollutants (TSS and Pb); however, permeable asphalt does not provided any retention of Cu and Zn, unlike permeable concrete. Therefore, if permeable pavements are to be used as a stormwater treatment method, it is recommended that permeable concrete be used instead. Modifying pavement design to improve stormwater quality can be an effective indirect method at treating atmospheric pollutants in stormwater.

Stormwater treatment systems that are implemented for removing atmospheric pollutants should target large rain events. This research determined that atmospheric pollutant wash-off during a rain event followed a logarithmic distribution (rain depth for dissolved pollutants and peak rain intensity and duration for particulate pollutants); therefore, as the rain event proceeded more pollutants are washed-off but the rate of this wash-off declined over time. Larger rain events (>10 mm) will have greater pollutant loads in runoff than smaller rain events; thus, capturing and treating larger rain events will provide better improvements to urban waterway quality.

Implementing effective measures to mitigate atmospheric deposition will be challenging unless effective legislation is brought into place minimising heavy metal emissions to the atmosphere particularly (i.e. source control). Implementing source controls on atmospheric heavy metal emissions in Christchurch cannot currently be done, as there is little information on atmospheric heavy metals sources; therefore, it is recommended that a source appointment study be undertaken so that legislative measures can be implemented. However, as discussed in this Thesis, transboundary pollution from Australia may be an important source of atmospheric heavy metals in Christchurch. In the instance where transboundary pollution is a significant source of atmospheric pollutants, local legislative measures will not be effective, as pollutants are transported from other regions beyond the legislative control. Until there is a global policy on reducing atmospheric pollutant emissions, local legislative measures in Christchurch (although, they should still occur) may not provide the best reduction to atmospheric pollutant loads in stormwater runoff. However, implementing legislation in areas that release high quantities of atmospheric metals pollutants will yield good reductions in atmospheric pollutant loads in stormwater. Until effective source control legislation is implemented, current focus should be on treating the stormwater runoff.

The information in this Thesis can be used to help stormwater managers in strategic decision-making processes such as choice of location and installation of different treatment systems.



## **8.2. Recommendations for future work**

### ***8.2.1. Polluting potential of asphalt***

An unexpected discovery from this research was that asphalt had the potential to release high quantities of pollutants: impermeable asphalt leached Zn; permeable asphalt leached acidity; and both pavements leached colour and surfactants. The bitumen and anti-stick foam used in the asphalt construction and transportation are the likely sources of the pollutants; however, this could not be definitively proven in this research. It is recommended that more research be conducted into the polluting potential of asphalt and bitumen. In particular, identifying the source of the pollution, i.e. the Zn, the low pH, colour and surfactants would be beneficial so pollutant mitigation techniques can be implemented. As discussed in the Thesis, the quality of the bitumen used for asphalt construction can vary from batch to batch; therefore, detailed chemical analyses on a selection of bitumen's from different oil fields and from different refining processes should be analysed.

Additionally, using asphalt derivatives (e.g. warm mix asphalt and rubber asphalt) in road infrastructure has increased in popularity (Hansen and Copeland 2013). Warm mix asphalt is an asphalt which is manufactured and spread at lower temperatures (100-140°C) to reduce the amount of greenhouse gas emissions produced (Rubio et al. 2012). Warm mixed asphalt is created by adding organic additives, chemical additives, or water-based surfactants that lowers the viscosity of bitumen, and thus, improves the workability of the asphalt (Rubio et al. 2012). It is recommended that runoff from warm mixed asphalt be analysed for pollutants. Rubber asphalt utilises crumbed rubber from old tyres in the asphalt mix. The benefits of adding rubber into the mix include greater pavement resistance to permanent deformation and reflective cracking, reduced noise, and; reduced thickness of asphalt overlays (Cong et al. 2013). The reuse of old tyres for rubber asphalt is considered an environmentally friendly and sustainable practice. However, only limited research has discussed the potential of Zn leaching from the crumbed rubber (Rhodes et al. 2012) but no research was found to discuss the potential of Zn to leach from the pavement itself. As tyres are considered a major source

of Zn to the urban environment (Davis et al. 2001), it is recommended that the effects of rubber asphalt on stormwater pollution be analysed.

#### ***8.2.2. Treatment performance of permeable pavements with varying pavement thickness***

In this research, 50 mm thick permeable asphalt and concrete was used to determine the performance of OGPA and PCon at retaining Cu, Zn, Pb, and TSS. However, no research was conducted on how varying the thickness of the permeable pavements influenced pollutant retention. It is assumed that increasing the permeable pavement thickness will result in increased pollutant retention, but by what quantity does the retention of pollutants increase remains unknown. It is recommended that experiments should be conducted with various pavement thicknesses (10 mm, 20 mm, 40 mm, 70 mm, and 100 mm) to determine how atmospheric pollutant retention varies with increasing pavement thickness.

#### ***8.2.3. Atmospheric pollutant wash-off from varying materials***

In this research, four different pavement types were monitored to determine their influence on atmospheric pollutant wash-off. However, pollutant wash-off from other materials was not analysed, for example, a galvanised steel roof, a slate roof, and a modular interlocking concrete pavement. It is recommended that experiments be conducted with various materials to determine their effect on atmospheric pollutant wash-off. This information would be used to better characterise the contribution of atmospheric deposition to stormwater pollution from a catchment area with varying surfaces.

#### ***8.2.4. Characterising the spatial variability of atmospheric deposition patterns***

It is recommended that the contribution of atmospheric deposition to stormwater pollution be monitored in more land-use areas. In this research, three land-use areas were studied, which is insufficient to characterise the spatial variability of atmospheric pollutant deposition to an entire urban airshed; although, this research has increased the understanding on this topic. Deploying the board setup to other areas would enable the spatial variability of the atmospheric deposition to be better characterised. In particular, emphasis should be placed on monitoring areas close to the ocean because it is assumed that the different wind patterns in these areas will result in different atmospheric deposition rates.

Additionally, in this research it was determined that the Ind site received greater deposition loads because it was located at the windward side of a slope. However, how deposition rates alter with distance from a hill slope remains unknown. It is recommended that bulk deposition samplers be located along a transit line away from a hill slope to determine how deposition rates changes with distance from a slope.

#### ***8.2.5. Characterising atmospheric deposition patterns for other airsheds***

Atmospheric deposition is an important contributor to stormwater pollution, but the extent of its contribution to stormwater will be dependent on the region studied. As atmospheric metal deposition in other cities is under researched, it is recommended that more studies on the dynamics of atmospheric deposition as a source of pollutants to stormwater be conducted.

#### ***8.2.6. Sources of atmospheric pollutants in Christchurch***

It is recommended that a source appointment study on atmospheric heavy metals pollution in Christchurch be conducted. Currently, there has been very little research on atmospheric heavy metal pollution, and thus, the principal emission source of heavy metals to the

Christchurch airshed remains unknown. This Thesis discussed the likelihood of pollution originating in Australia being transported to Christchurch. It is recommended that research be conducted into this possibility through  $^{210}\text{Pb}$  isotope analyses (see Marx et al. (2008) for more details).

#### ***8.2.7. Effect of wind on atmospheric deposition***

In this research, determining the influence of wind on atmospheric deposition was difficult due to the methodology employed – wind speed and direction was averaged over the entire antecedent dry period. Therefore, using a single value to represent wind speed and direction was not suitable for determining its effect on pollutant build-up. It is recommended that more research into wind and atmospheric deposition be conducted in the future. A potential method for monitoring the effect of wind on atmospheric deposition would be to collect particulate matter by a vacuum. The pavement boards would be exposed for a set period (<1 day) – the particulate matter deposited on the boards would be vacuumed into a collection bottle and the contents weighed. During the period when the boards are exposed, wind speed and direction should be accurately measured. Models can be derived which can take into account the average wind speed and direction during the experiment and the mass of particulates deposited. Therefore, the influence of wind on atmospheric deposition can be more accurately estimated.

In addition, wind speed also influences particulate resuspension. Although, the pavement board setup enabled resuspension to occur, resuspension was not directly quantified in this research. Therefore, the extent of particulate loss via resuspension remains unknown. To quantify resuspension, it is suggested that the research be conducted in a wind tunnel where the wind speed could be controlled. Boards with a known quantity of particulates applied would be exposed to varying wind speeds so resuspension can occur. The amount of particulates remaining on the boards after the experiment could be quantified (possibly with a vacuum collector). Changes to particulate mass would be a result of particulate resuspension, and thus, resuspension at varying wind speed can be analysed.

#### ***8.2.8. A web-based model predicting atmospheric pollutant loads in stormwater***

It is recommended that the information provided in this research be used to develop a web-based model on atmospheric pollutant loads in stormwater from various pavement types. The model would be freely available to stormwater managers. The web-based would be developed from a simple regression model predicting bulk deposition loads. Stormwater modelers can then input the necessary criteria (e.g. number of antecedent dry days and rain depth) into the regression model. The output would be a prediction of the atmospheric pollutant loads in stormwater runoff. Factors will be applied to the predicted load to account for pollutant retention from different pavement types and to account for variations in deposition rates due to location by a windward slope. Therefore, stormwater modelers can better estimate the contribution of atmospheric deposition when modelling stormwater quality, which will overall improve the accuracy of their models.

## REFERENCES

- Abustan, I., Hamzah, M. O., & Rashid, M. A. (2012). Review of permeable pavement systems in Malaysia conditions. *OIDA International Journal of Sustainable Development*, 4(2), 27-36.
- Adachi, K., & Tainosho, Y. (2004). Characterization of heavy metal particles embedded in tire dust. *Environment International*, 30, 1009-1017, doi:<http://dx.doi.org/10.1016/j.envint.2004.04.004>.
- Adriano, D. C. (2001). *Trace elements in terrestrial environments: biogeochemistry, bioavailability, and risks of metals* (2nd edition ed., Vol. 2nd Edition). New York: Springer-Verlag.
- Akaike, H. (1998). Information theory and an extension of the maximum likelihood principle. In E. Parzen, K. Tanabe, & G. Kitagawa (Eds.), *Selected Papers of Hirotugu Akaike* (pp. 199-213, Springer Series in Statistics): Springer New York.
- Amann, M., Bertok, I., Cofala, J., Gyarfas, F., Heyes, C., Klimont, Z., et al. (2005). Baseline scenarios for the clean air for Europe (CAFE) programme. (Vol. B4-3040/2002/340248/MAR/C1). Laxenburg, Austria: European Commission - Directorate General for the Environment.
- ANZECC (2000). Australian and New Zealand guidelines for fresh and marine water quality. Australian and New Zealand Environment and Conservation Council.
- APHA (2005). Standard methods for the examination of water and wastewater. (21th ed.). Washington D.C.: American Public Health Association.
- Arnold, C. L., & Gibbons, C. J. (1996). Impervious surface coverage: the emergence of a key environmental indicator. *Journal of the American Planning Association*, 62(2), 243-258, doi:10.1080/01944369608975688.
- Aryal, R., Kandasamy, J., Vigneswaran, S., Naidu, R., & Lee, S. H. (2009). Review of stormwater quality, quantity and treatment methods part 1: stormwater quantity modelling. *Environmental Engineering Research*, 14(2), 71-78.
- Aryal, R., Vigneswaran, S., Kandasamy, J., & Naidu, R. (2010). Urban stormwater quality and treatment. *Korean Journal of Chemical Engineering*, 27(5), 1343-1359, doi:10.1007/s11814-010-0387-0.
- Auckland Council. Permeable pavement construction guide stormwater device information series. Auckland Council.
- Auckland Regional Council (2003). Technical publication 10, design guideline manual: stormwater treatment device. Auckland Regional Council.
- Auckland Regional Council (2005). Sources and loads of metals in urban stormwater. *Technical Publication No. ARC04104*.
- Awan, M., Ahmed, S. H., Aslam, M. R., Qazi, I., & Baig, M. A. (2013). Determination of heavy metals in ambient air particulate matter using laser-induced breakdown spectroscopy. *Arabian Journal for Science and Engineering*, 38(7), 1655-1661, doi:10.1007/s13369-013-0548-7.
- Azimi, S., Ludwig, A., Thévenot, D. R., & Colin, J.-L. (2003). Trace metal determination in total atmospheric deposition in rural and urban areas. *Science of the Total Environment*, 308(1-3), 247-256, doi:10.1016/s0048-9697(02)00678-2.

- Aziz, H. A., Othman, N., Yusuff, M. S., Basri, D. R. H., Ashaari, F. A. H., Adlan, M. N., et al. (2001). Removal of copper from water using limestone filtration technique: determination of mechanism of removal. *Environment International*, 26(5–6), 395–399, doi:[http://dx.doi.org/10.1016/S0160-4120\(01\)00018-6](http://dx.doi.org/10.1016/S0160-4120(01)00018-6).
- Bahar, B., Herting, G., Wallinder, I., Hakkila, K., Leygraf, C., & Virta, M. (2008). The interaction between concrete pavement and corrosion-induced copper runoff from buildings. *Environmental Monitoring and Assessment*, 140(1), 175–189, doi:10.1007/s10661-007-9858-0.
- Balades, J. D., Legret, M., & Madiec, H. (1995). *Permeable pavements: pollution management tools*. Paper presented at the Proceedings of the 1995 2nd NOVATECH Conference on Innovative Technologies in Urban Storm Drainage, May 30, 1995 - June 1, 1995, Lyon, Fr,
- Bannerman, R. T., Owens, D. W., Dodds, R. B., & Hornewer, N. J. (1993). Sources of pollutants in Wisconsin stormwater. *Water Science & Technology*, 28(3-5), 241–259.
- Barrett, M., Jr., L., Jr., J., & Charbeneau, R. (1998). Characterization of highway runoff in Austin, Texas, area. *Journal of Environmental Engineering*, 124(2), 131–137, doi:10.1061/(ASCE)0733-9372(1998)124:2(131).
- Barrett, M. E. (2008). Effects of a permeable friction course on highway runoff. *Journal of Irrigation and Drainage Engineering*, 134(5), 646–651, doi:10.1061/(asce)0733-9437(2008)134:5(646).
- Barrett, M. E., Kearfott, P., & Malina, J. F., Jr. (2006). Stormwater quality benefits of a porous friction course and its effect on pollutant removal by roadside shoulders. *Water Environment Research*, 78(11), 2177–2185, doi:10.2307/25053618.
- Barrett, M. E., & Shaw, C. B. (2007). Benefits of porous asphalt overlay on storm water quality. *Transportation Research Record*, 127–134, doi:10.3141/2025-13.
- Barrett, M. E., Zuber, R. D., Collins, E. R., Malina, J. F., Charbeneau, R. J., & Ward, G. H. (1995). A review and evaluation of literature pertaining to the quantity and control of pollution from highway runoff and construction. *CWRW Online Report 95-5*: Centre for Research in Water Resources.
- Barry, M. (2006). Stormwater pollution: is it damaging urban waterways? *Australasian Science* (Vol. 27, pp. 38–41). Hawksburn, Australia, Hawksburn.
- Barton, K. (2014). MuMIn: Multi-model inference. *R package version 1.10.0*. <http://CRAN.R-project.org/package=MuMIn>.
- Bates, D., Maechler, M., Bolker, B., & Walker, S. (2014). lme4: Linear mixed-effects models using Eigen and S4. R package version 1.1–6.
- Beasley, G., & Kneale, P. (2002). Reviewing the impact of metals and PAHs on macro invertebrates in urban watercourses. *Progress in Physical Geography*, 26(2), 236–270, doi:10.1191/0309133302pp334ra.
- Beck, H. J., & Birch, G. F. (2011). Spatial and temporal variance of metal and suspended solids relationships in urban stormwater-implications for monitoring. *Water, Air & Soil Pollution*, 223(3), 1–11, doi:10.1007/s11270-011-0919-1.
- Beck, H. J., & Birch, G. F. (2013). The magnitude of variability produced by methods used to estimate annual stormwater contaminant loads for highly urbanised catchments. *Environmental Monitoring & Assessment*, 185(6), 5209–5220, doi:10.1007/s10661-012-2937-x.

- Beilke, S., Elshout, A. J., & Commission of the European Communities (1983). *Acid deposition: proceedings of the CEC workshop organized as part of the concerted action "physico-chemical behaviour of atmospheric pollutants", held in Berlin, 9 September 1982*: Reidel.
- Berger, J., & Denby, B. (2011). A generalised model for traffic induced road dust emissions. Model description and evaluation. *Atmospheric Environment*, 45(22), 3692-3703, doi:<http://dx.doi.org/10.1016/j.atmosenv.2011.04.021>.
- Berhanu Desta, M., Bruen, M., Higgins, N., & Johnston, P. (2007). Highway runoff quality in Ireland. *Journal of Environmental Monitoring*, 9(4), 366-371, doi:10.1039/b702327h.
- Bernot, M. J., Calkins, M., Bernot, R. J., & Hunt, M. (2011). The influence of different urban pavements on water chemistry. *Road Materials and Pavement Design*, 12(1), 159-176, doi:10.1080/14680629.2011.9690357.
- Birch, H., Vezzaro, L., & Mikkelsen, P. S. (2013). Model-based monitoring of stormwater runoff quality. *Water Science & Technology*, 68(5), 1063-1071, doi:10.2166/wst.2013.348.
- Birmili, W., Allen, A. G., Bary, F., & Harrison, R. M. (2006). Trace metal concentrations and water solubility in size-fractionated atmospheric particles and influence of road traffic. *Environmental Science & Technology*, 40(4), 1144-1153, doi:10.1021/es0486925.
- Booth, D. B., & Jackson, C. R. (1997). Urbanization of aquatic systems: degradation thresholds, stormwater detection, and the limits of mitigation *Journal of the American Water Resources Association*, 33(5), 1077-1090, doi:10.1111/j.1752-1688.1997.tb04126.x.
- Booth, D. B., & Leavitt, J. (1999). Field evaluation of permeable pavement systems for improved stormwater management. *Journal of the American Planning Association*, 65(3), 314-325, doi:10.1080/01944369908976060.
- Boulanger, B., & Nikolaidis, N. P. (2003). Mobility and aquatic toxicity of copper in an urban watershed. *JAWRA Journal of the American Water Resources Association*, 39(2), 325-336, doi:10.1111/j.1752-1688.2003.tb04387.x.
- Boving, T. B., Stolt, M. H., Augenstern, J., & Brosnan, B. (2008). Potential for localized groundwater contamination in a porous pavement parking lot setting in Rhode Island. *Environmental geology (Berlin)*, 55(3), 571-582, doi:10.1007/s00254-007-1008-z.
- Bramer, L. (2007). Instantaneous-profile laser scanner: user's manual. In J. Frankenberger (Ed.).
- Brandt, H. C. A., & de Groot, P. C. (2001). Aqueous leaching of polycyclic aromatic hydrocarbons from bitumen and asphalt. *Water Research*, 35(17), 4200-4207, doi:[http://dx.doi.org/10.1016/S0043-1354\(01\)00216-0](http://dx.doi.org/10.1016/S0043-1354(01)00216-0).
- Brattebo, B. O., & Booth, D. B. (2003). Long-term stormwater quantity and quality performance of permeable pavement systems. *Water Research*, 37(18), 4369-4376, doi:10.1016/s0043-1354(03)00410-x.
- Brezonik, P. L., & Stadelmann, T. H. (2002). Analysis and predictive models of stormwater runoff volumes, loads, and pollutant concentrations from watersheds in the Twin Cities metropolitan area, Minnesota, USA. *Water Research*, 36(7), 1743-1757, doi:[http://dx.doi.org/10.1016/S0043-1354\(01\)00375-X](http://dx.doi.org/10.1016/S0043-1354(01)00375-X).
- Bringmark, L., Lundin, L., Augustaitis, A., Beudert, B., Dieffenbach-Fries, H., Dirnböck, T., et al. (2013). Trace metal budgets for forested catchments in Europe—Pb, Cd, Hg, Cu and Zn. *Water, Air, & Soil Pollution*, 224(4), 1-14, doi:10.1007/s11270-013-1502-8.



- Brown, R. R., Farrelly, M. A., & Loorbach, D. A. (2013). Actors working the institutions in sustainability transitions: the case of Melbourne's stormwater management. *Global Environmental Change*, 23(4), 701-718, doi:<http://dx.doi.org/10.1016/j.gloenvcha.2013.02.013>.
- Bullin, J. A., & Moe, R. D. (1982). Measurement and analysis of aerosols along Texas roadways. *Environmental Science & Technology*, 16(4), 197-202, doi:10.1021/es00098a005.
- Burian, S. J., Streit, G. E., McPherson, T. N., Brown, M. J., & Turin, H. J. (2001). Modeling the atmospheric deposition and stormwater washoff of nitrogen compounds. *Environmental Modelling & Software*, 16(5), 467-479, doi:10.1016/s1364-8152(01)00027-5.
- Camponelli, K. M., Lev, S. M., Snodgrass, J. W., Landa, E. R., & Casey, R. E. (2010). Chemical fractionation of Cu and Zn in stormwater, roadway dust and stormwater pond sediments. *Environmental Pollution*, 158(6), 2143-2149, doi:<http://dx.doi.org/10.1016/j.envpol.2010.02.024>.
- Cao, Z., Yang, Y., Lu, J., & Zhang, C. (2011). Atmospheric particle characterization, distribution, and deposition in Xi'an, Shaanxi Province, Central China. *Environmental Pollution*, 159(2), 577-584, doi:<http://dx.doi.org/10.1016/j.envpol.2010.10.006>.
- CCANZ (2013). Benefits of building concrete roads in New Zealand: a backgrounder. Wellington, New Zealand.
- CCC (2003). Waterways, wetlands and drainage guide = Ko te anga whakaora mō ngā arawai rēpō: Part B. Christchurch: Christchurch City Council.
- CCC (2006). State of the environment monitoring: air quality. [http://resources.ccc.govt.nz/files/AirQuality\\_2115\\_EmissionsInventory-docs.pdf](http://resources.ccc.govt.nz/files/AirQuality_2115_EmissionsInventory-docs.pdf). Accessed 13/10/2014.
- CCC (2011). Ambient air quality. [http://resources.ccc.govt.nz/files/AirQuality\\_1040\\_PM10Exceedences-docs.pdf](http://resources.ccc.govt.nz/files/AirQuality_1040_PM10Exceedences-docs.pdf). Accessed 13/10/2014.
- Characklis, G., & Wiesner, M. (1997). Particles, metals, and water quality in runoff from large urban watershed. *Journal of Environmental Engineering*, 123(8), 753-759, doi:10.1061/(ASCE)0733-9372(1997)123:8(753).
- Charbeneau, R. J., & Barrett, M. E. (1998). Evaluation of methods for estimating stormwater pollutant loads. *Water Environment Research*, 70(7), 1295-1302, doi:10.2307/25045155.
- Chen, J., & Adams, B. (2006). Analytical urban storm water quality models based on pollutant buildup and washoff processes. *Journal of Environmental Engineering*, 132(10), 1314-1330, doi:10.1061/(ASCE)0733-9372(2006)132:10(1314).
- Chen, L., Peng, S., Liu, J., & Hou, Q. (2012). Dry deposition velocity of total suspended particles and meteorological influence in four locations in Guangzhou, China. *Journal of Environmental Sciences*, 24(4), 632-639, doi:[http://dx.doi.org/10.1016/S1001-0742\(11\)60805-X](http://dx.doi.org/10.1016/S1001-0742(11)60805-X).
- Chester, R., Nimmo, M., & Preston, M. R. (1999). The trace metal chemistry of atmospheric dry deposition samples collected at Cap Ferrat: a coastal site in the Western Mediterranean. *Marine Chemistry*, 68(1-2), 15-30, doi:[http://dx.doi.org/10.1016/S0304-4203\(99\)00062-6](http://dx.doi.org/10.1016/S0304-4203(99)00062-6).

- Chin, A. (2006). Urban transformation of river landscapes in a global context. *Geomorphology*, 79(3–4), 460–487, doi:<http://dx.doi.org/10.1016/j.geomorph.2006.06.033>.
- Chow, M. F., Yusop, Z., & Abustan, I. (2013). Relationship between sediment build-up characteristics and antecedent dry days on different urban road surfaces in Malaysia. *Urban Water Journal*, 1–8, doi:10.1080/1573062x.2013.839718.
- Chu-Fang, W., Cheng-Yuan, C., Su-Fen, T., & Hung-Lung, C. (2005). Characteristics of road dust from different sampling sites in Northern Taiwan. *Journal of the Air & Waste Management Association*, 55(8), 1236–1244.
- Clark, S. E., Steele, K. A., Spicher, J., Siu, C. Y. S., Lalor, M. M., Pitt, R., et al. (2008). Roofing materials' contributions to storm-water runoff pollution. *Journal of Irrigation and Drainage Engineering*, 134(5), 638–645.
- Coe, R. (2002). *It's the effect size, stupid: what effect size is and why it is important*. Paper presented at the Annual Conference of the British Educational Research Association, England, 12–14 September, 2002.
- Cohen, J. (1988). *Statistical power analysis for the behavioral sciences* (2ed.). New Jersey: Lawrence Erlbaum Associates.
- Colin, J. L., Jaffrezo, J. L., & Gros, J. M. (1990). Solubility of major species in precipitation: factors of variation. *Atmospheric Environment. Part A. General Topics*, 24(3), 537–544, doi:[http://dx.doi.org/10.1016/0960-1686\(90\)90008-B](http://dx.doi.org/10.1016/0960-1686(90)90008-B).
- Collins, F. (2010). Inclusion of carbonation during the life cycle of built and recycled concrete: influence on their carbon footprint. *The International Journal of Life Cycle Assessment*, 15(6), 549–556, doi:10.1007/s11367-010-0191-4.
- Cong, P., Xun, P., Xing, M., & Chen, S. (2013). Investigation of asphalt binder containing various crumb rubbers and asphalts. *Construction and Building Materials*, 40(0), 632–641, doi:<http://dx.doi.org/10.1016/j.conbuildmat.2012.11.063>.
- Conko, K. M., Rice, K. C., & Kennedy, M. M. (2004). Atmospheric wet deposition of trace elements to a suburban environment, Reston, Virginia, USA. *Atmospheric Environment*, 38(24), 4025–4033, doi:<http://dx.doi.org/10.1016/j.atmosenv.2004.03.062>.
- Corsmeier, U., Kossmann, M., Kalthoff, N., & Sturman, A. (2006). Temporal evolution of winter smog within a nocturnal boundary layer at Christchurch, New Zealand. *Meteorology and Atmospheric Physics*, 91(1–4), 129–148, doi:10.1007/s00703-005-0111-5.
- Crabtree, B., Moy, F., Whitehead, M., & Roe, A. (2006). Monitoring pollutants in highway runoff. *Water and Environment Journal*, 20(4), 287–294, doi:10.1111/j.1747-6593.2006.00033.x.
- CRPS (2013). Canterbury regional policy statement 2013. Environment Canterbury.
- Darboux, F., & Huang, C.-h. (2003). An instantaneous-profile laser scanner to measure soil surface microtopography. *Soil Sci. Soc. Am. J.*, 67(1), 92–99, doi:10.2136/sssaj2003.9200.
- Davidson, C. I., & Wu, Y.-L. (1990). Dry deposition of particles and vapors. In S. E. Lindberg, A. L. Page, & S. A. Norton (Eds.), *Acidic Precipitation: Sources, Deposition, and Canopy Interactions* (Advances in Environmental Science Vol. 3). New York: Springer-Verlag.

- Davis, A. P., Shokouhian, M., & Ni, S. (2001). Loading estimates of lead, copper, cadmium, and zinc in urban runoff from specific sources. *Chemosphere*, 44(5), 997-1009, doi:10.1016/s0045-6535(00)00561-0.
- Davis, A. P., Traver, R. G., & Hunt, W. F. (2010a). Improving urban stormwater quality: applying fundamental principles. *Journal of Contemporary Water Research & Education*, 146(1), 3-10, doi:10.1111/j.1936-704X.2010.00387.x.
- Davis, B. S., & Birch, G. F. (2011). Spatial distribution of bulk atmospheric deposition of heavy metals in metropolitan Sydney, Australia. *Water, Air & Soil Pollution*, 214(1-4), 147-162, doi:10.1007/s11270-010-0411-3.
- Davis, P. J., Wright, I. A., Jonasson, O. J., & Findlay, S. J. (2010b). Impact of concrete and PVC pipes on urban water chemistry. *Urban Water Journal*, 7(4), 233-241.
- Davy, P., Trompetter, B., & Markwitz, A. (2011). Concentration, composition and sources of particulate matter in the Johnstone's Hill Tunnel, Auckland. *GNS Science Consultancy Report 2010/296* (pp. 60).
- Deboudt, K., Flament, P., & Bertho, M.-L. (2004). Cd, Cu, Pb and Zn concentrations in atmospheric wet deposition at a coastal station in Western Europe. *Water, air, and soil pollution*, 151(1-4), 335-359, doi:10.1023/b:wate.0000009906.55895.30.
- Deletic, A., & Maksimovic, C. (1998). Evaluation of water quality factors in storm runoff from paved areas. *Journal of Environmental Engineering*, 124(9), 869-879, doi:10.1061/(ASCE)0733-9372(1998)124:9(869).
- Dierkes, C., Holte, A., & Geiger, W. F. (1999). *Heavy metal retention within a porous pavement structure*. Paper presented at the 8th International Conference on Urban Storm Drainage, Sydney, Australia, 1999.
- Dierkes, C., Kuhlmann, L., Kandasamy, J., & Angelis, G. (2002). *Pollution retention capability and maintenance of permeable pavements*. Paper presented at the Proceedings of the Global Solutions for Urban Drainage, Ninth International Conference on Urban Drainage, Portland, OR, September 8-13, 2002.
- Driver, N. E., & Tasker, G. D. (1990). Techniques for estimation of storm-runoff loads, volumes, and selected constituent concentrations in urban watersheds in the United States. *U.S. Geol. Surv. Water Supply Pap. 2363* (Vol. 44).
- Duda, A. M., Lenat, D. R., & Penrose, D. L. (1982). Water quality in urban streams - what we can expect. *Journal (Water Pollution Control Federation)*, 54(7), 1139-1147.
- Duncan, H. P. (1995). A review of urban stormwater quality processes: Report 95/5. Cooperative Research Centre for Catchment Hydrology.
- Dunne, T., & Leopold, L. B. (1978). *Water in environmental planning*. San Francisco: W. H. Freeman & Company.
- ECan (2007). Literature review: urban river contaminants. Christchurch: Environment Canterbury.
- ECan (2011). Canterbury water - the regional context: supporting the Canterbury Water Management Strategy.
- Eck, B., Winston, R., Hunt, W., & Barrett, M. (2012). Water quality of drainage from permeable friction course. *Journal of Environmental Engineering*, 138(2), 174-181, doi:doi:10.1061/(ASCE)EE.1943-7870.0000476.
- Egodawatta, P., & Goonetilleke, A. (2008a). *Modelling pollutant build-up and wash-off in urban road and roof surfaces*. Paper presented at the 31st Hydrology and Water

- Resources Symposium and the 4th International Conference on Water Resources and Environment Research, Engineers Australia, Adelaide, Australia, 2008.
- Egodawatta, P., Thomas, E., & Goonetilleke, A. (2007). Mathematical interpretation of pollutant wash-off from urban road surfaces using simulated rainfall. *Water Research*, 41(13), 3025-3031, doi:10.1016/j.watres.2007.03.037.
- Egodawatta, P., Thomas, E., & Goonetilleke, A. (2009). Understanding the physical processes of pollutant build-up and wash-off on roof surfaces. *Science of the Total Environment*, 407(6), 1834-1841, doi:10.1016/j.scitotenv.2008.12.027.
- Egodawatta, P. K., & Goonetilleke, A. (2008b). Understanding urban road surface pollutant wash-off and underlying physical processes using simulated rainfall. *Water Science & Technology*, 57(8), 1241-1246, doi:10.2166/wst.2008.260.
- Ellis, J. B., & Harrop, D. O. (1984). Variations in solids loadings to roadside gully pots. *Science of the Total Environment*, 33(1-4), 203-211, doi:[http://dx.doi.org/10.1016/0048-9697\(84\)90394-2](http://dx.doi.org/10.1016/0048-9697(84)90394-2).
- Ellis, J. B., Harrop, D. O., & Revitt, D. M. (1986). Hydrological controls of pollutant removal from highway surfaces. *Water Research*, 20(5), 589-595, doi:[http://dx.doi.org/10.1016/0043-1354\(86\)90023-0](http://dx.doi.org/10.1016/0043-1354(86)90023-0).
- Erickson, T. O., & Stefan, H. G. (2009). Natural groundwater recharge response to urbanization: Vermillion River watershed, Minnesota. *Journal of Water Resources Planning and Management*, 135(6), 512-520.
- Erisman, J. W., & Draaijers, G. (2003). Deposition to forests in Europe: Most important factors influencing dry deposition and models used for generalisation. *Environmental Pollution*, 124(3), 379-388, doi:[http://dx.doi.org/10.1016/S0269-7491\(03\)00049-6](http://dx.doi.org/10.1016/S0269-7491(03)00049-6).
- Espey, W. H., Jr., Morgan, C. W., & Masch, F. D. (1966). A study of some effects of urbanization on storm runoff from a small watershed. (Vol. Report 23). United States, Texas: Texas Water Development Board.
- ESRI (2013). ArcMap 10.2. Redlands, California: Environmental Systems Research Institute.
- European Commission (2014). Introduction to the new EU Water Framework Directive [http://ec.europa.eu/environment/water/water-framework/info/intro\\_en.htm](http://ec.europa.eu/environment/water/water-framework/info/intro_en.htm). Accessed 08/04/2014.
- Fang, G.-C., Wu, Y.-S., Lee, W.-J., Chou, T.-Y., & Lin, I. C. (2007a). Ambient air particulates, metallic elements, dry deposition and concentrations at Taichung Airport, Taiwan. *Atmospheric Research*, 84(3), 280-289, doi:<http://dx.doi.org/10.1016/j.atmosres.2006.08.006>.
- Fang, G.-C., Wu, Y.-S., Lee, W.-J., Chou, T.-Y., & Lin, I. C. (2007b). Study of ambient air particulates pollutants near Taichung airport sampling site in central Taiwan. *Journal of Hazardous Materials*, 144(1-2), 492-498, doi:10.1016/j.jhazmat.2006.10.064.
- Fang, G. C. (1998). Dry deposition of atmospheric pollutants in Taiwan. *Journal of Environmental Science and Health, Part A*, 33(8), 1803-1823, doi:10.1080/10934529809376819.
- Farahmand, T., Fleming, S. W., & Quilty, E. J. (2007). Detection and visualization of storm hydrograph changes under urbanization: An impulse response approach. *Journal of Environmental Management*, 85(1), 93-100, doi:10.1016/j.jenvman.2006.08.004.
- Fassman, E. A., & Blackbourn, S. (2010). Urban runoff mitigation by a permeable pavement system over impermeable soils. *Journal of Hydrologic Engineering*, 15(6), 475-485, doi:10.1061/(asce)he.1943-5584.0000238.

- Fassman, E. A., & Blackbourn, S. D. (2011). Road runoff water-quality mitigation by permeable modular concrete pavers. *Journal of Irrigation and Drainage Engineering-Asce*, 137(11), 720-729, doi:10.1061/(asce)ir.1943-4774.0000339.
- Field, A. (2013). *Discovering statistics using IBM SPSS Statistics* (4th ed.). London: SAGE Publications Ltd.
- Fletcher, T., Duncan, H., Poelsma, P., & Lloyd, S. (2004). Stormwater flow and quality, and the effectiveness of non-proprietary stormwater treatment measures - A review and gap analysis. In Cooperative Research Centre for Catchment Hydrology (Ed.). Sydney: Monash University.
- Freydier, R., Dupre, B., & Lacaux, J. P. (1998). Precipitation chemistry in intertropical Africa. *Atmospheric Environment*, 32(4), 749-765, doi:[http://dx.doi.org/10.1016/S1352-2310\(97\)00342-7](http://dx.doi.org/10.1016/S1352-2310(97)00342-7).
- Galloway, J. N., Thornton, J. D., Norton, S. A., Volchok, H. L., & McLean, R. A. N. (1982). Trace metals in atmospheric deposition: A review and assessment. *Atmospheric Environment* (1967), 16(7), 1677-1700, doi:10.1016/0004-6981(82)90262-1.
- Gan, H., Zhuo, M., Li, D., & Zhou, Y. (2008). Quality characterization and impact assessment of highway runoff in urban and rural area of Guangzhou, China. *Environmental Monitoring and Assessment*, 140(1-3), 147-159, doi:10.1007/s10661-007-9856-2.
- Garg, B. D., Cadle, S. H., Mulawa, P. A., Groblicki, P. J., Laroo, C., & Parr, G. A. (2000). Brake wear particulate matter emissions. *Environmental Science & Technology*, 34(21), 4463-4469, doi:10.1021/es001108h.
- Garnaud, S., Mouchel, J.-M., Chebbo, G., & Thévenot, D. R. (1999). Heavy metal concentrations in dry and wet atmospheric deposits in Paris district: comparison with urban runoff. *Science of the Total Environment*, 235(1-3), 235-245, doi:[http://dx.doi.org/10.1016/S0048-9697\(99\)00199-0](http://dx.doi.org/10.1016/S0048-9697(99)00199-0).
- Göbel, P., Dierkes, C., & Coldewey, W. G. (2007). Storm water runoff concentration matrix for urban areas. *Journal of Contaminant Hydrology*, 91(1-2), 26-42, doi:10.1016/j.jconhyd.2006.08.008.
- González-Miqueo, L., Elustondo, D., Lasheras, E., Bermejo, R., & Santamaría, J. M. (2009). Spatial trends in heavy metals and nitrogen deposition in Navarra (Northern Spain) based on moss analysis. *Journal of Atmospheric Chemistry*, 62(1), 59-72, doi:10.1007/s10874-009-9139-0.
- Good, J. (2011). *Water quality treatment and hydraulic efficacy of laboratory and field rain gardens* University of Canterbury, Christchurch.
- Goossens, D. (1988). The effect of surface curvature on the deposition of loess: a physical model. *CATENA*, 15(2), 179-194, doi:[http://dx.doi.org/10.1016/0341-8162\(88\)90027-6](http://dx.doi.org/10.1016/0341-8162(88)90027-6).
- Goossens, D. (1996). Wind tunnel experiments of aeolian dust deposition along ranges of hills. *Earth Surface Processes and Landforms*, 21(3), 205-216, doi:10.1002/(sici)1096-9837(199603)21:3<205::aid-esp505>3.0.co;2-t.
- Grantz, D. A., Garner, J. H. B., & Johnson, D. W. (2003). Ecological effects of particulate matter. *Environment International*, 29(2-3), 213-239, doi:[http://dx.doi.org/10.1016/S0160-4120\(02\)00181-2](http://dx.doi.org/10.1016/S0160-4120(02)00181-2).
- Gray, C. W., McLaren, R. G., & Roberts, A. H. C. (2003). Atmospheric accessions of heavy metals to some New Zealand pastoral soils. *Science of the Total Environment*, 305(1-3), 105-115, doi:[http://dx.doi.org/10.1016/S0048-9697\(02\)00404-7](http://dx.doi.org/10.1016/S0048-9697(02)00404-7).



- Gunawardena, J., Egodawatta, P., Ayoko, G. A., & Goonetilleke, A. (2011). *Atmospheric deposition as a source of stormwater pollution in Gold Coast, Australia*. Paper presented at the Proceedings of the 34th IAHR World Congress, 33rd Hydrology and Water Resources Symposium and 10th Conference on Hydraulics in Water Engineering, Brisbane, Australia, 2011.
- Gunawardena, J., Egodawatta, P., Ayoko, G. A., & Goonetilleke, A. (2013). Atmospheric deposition as a source of heavy metals in urban stormwater. *Atmospheric Environment*, 68, 235-242, doi:<http://dx.doi.org/10.1016/j.atmosenv.2012.11.062>.
- Gupta, K., & Saul, A. J. (1996). Specific relationships for the first flush load in combined sewer flows. *Water Research*, 30(5), 1244-1252, doi:[http://dx.doi.org/10.1016/0043-1354\(95\)00282-0](http://dx.doi.org/10.1016/0043-1354(95)00282-0).
- Gurnell, A., Lee, M., & Souch, C. (2007). Urban rivers: hydrology, geomorphology, ecology and opportunities for change. *Geography Compass*, 1(5), 1118-1137, doi:10.1111/j.1749-8198.2007.00058.x.
- Halstead, M. J. R., Cunninghame, R. G., & Hunter, K. A. (2000). Wet deposition of trace metals to a remote site in Fiordland, New Zealand. *Atmospheric Environment*, 34(4), 665-676, doi:[http://dx.doi.org/10.1016/S1352-2310\(99\)00185-5](http://dx.doi.org/10.1016/S1352-2310(99)00185-5).
- Han, Y., Lau, S.-L., Kayhanian, M., & Stenstrom, M. K. (2006). Characteristics of highway stormwater runoff. *Water Environment Research*, 78(12), 2377-2388, doi:10.2175/106143006x95447.
- Hansen, K. R., & Copeland, A. (2013). Annual asphalt pavement industry survey on recycled materials and warm-mix asphalt usage: 2009–2012. Maryland, U.S.: National Asphalt Pavement Association.
- Harrison, R. M., & Johnston, W. R. (1985). Deposition fluxes of lead, cadmium, copper and polynuclear aromatic hydrocarbons (PAH) on the verges of a major highway. *Science of the Total Environment*, 46, 121-135.
- Harrison, R. M., & Wilson, S. J. (1985). The chemical composition of highway drainage waters I. Major ions and selected trace metals. *Science of the Total Environment*, 43(1–2), 63-77, doi:[http://dx.doi.org/10.1016/0048-9697\(85\)90031-2](http://dx.doi.org/10.1016/0048-9697(85)90031-2).
- Haselbach, L., Poor, C., & Tilson, J. (2014). Dissolved zinc and copper retention from stormwater runoff in ordinary portland cement pervious concrete. *Construction and Building Materials*, 53, 652-657, doi:<http://dx.doi.org/10.1016/j.conbuildmat.2013.12.013>.
- Haster, T., & James, W. (1994). Predicting sediment yield in storm-water runoff from urban areas. *Journal of Water Resources Planning & Management*, 120(5), 630-650, doi:10.1061/(ASCE)0733-9496(1994)120:5(630).
- He, W., Odnevall Wallinder, I., & Leygraf, C. (2001). A laboratory study of copper and zinc runoff during first flush and steady-state conditions. *Corrosion Science*, 43(1), 127-146, doi:10.1016/s0010-938x(00)00066-4.
- Hendry, C. D., & Brezonik, P. L. (1980). Chemistry of precipitation at Gainesville, Florida. *Environmental Science & Technology*, 14(7), 843-849, doi:10.1021/es60167a008.
- Hewitt, C. N., & Rashed, M. B. (1992). Removal rates of selected pollutants in the runoff waters from a major rural highway. *Water Research*, 26(3), 311-319, doi:[http://dx.doi.org/10.1016/0043-1354\(92\)90028-3](http://dx.doi.org/10.1016/0043-1354(92)90028-3).

- Hjortenkrans, D. S. T., Bergbäck, B. G., & Häggerud, A. V. (2007). Metal emissions from brake linings and tires: case studies of Stockholm, Sweden 1995/1998 and 2005. *Environmental Science & Technology*, 41(15), 5224-5230, doi:10.1021/es070198o.
- Hoffman, E. J., Latimer, J. S., Mills, G. L., & Quinn, J. G. (1982). Petroleum hydrocarbons in urban runoff from a commercial land use area. *Journal (Water Pollution Control Federation)*, 54(11), 1517-1525, doi:10.2307/25041743.
- Horvath, A., & Hendrickson, C. (1998). Comparison of environmental implications of asphalt and steel-reinforced concrete pavements. *Transportation Research Record: Journal of the Transportation Research Board*, 1626, 105-113, doi:10.3141/1626-13.
- Hou, H., Takamatsu, T., Koshikawa, M. K., & Hosomi, M. (2005). Trace metals in bulk precipitation and throughfall in a suburban area of Japan. *Atmospheric Environment*, 39(20), 3583-3595, doi:10.1016/j.atmosenv.2005.02.035.
- Hu, G. P., & Balasubramanian, R. (2003). Wet deposition of trace metals in Singapore. *Water, air, and soil pollution*, 144(1), 285-300.
- Huber, G. (2000). *Performance survey on open-graded friction course mixes* (National Cooperative Highway Research Program, Synthesis of Highway Practice 284). Washington D.C., U.S.: Transportation Research Board.
- Huber, W. C., & Dickinson, R. E. (1988). Storm water management model. *User's Manual Version 4 Rep. EPA/600/3-88/001a*. Athens, Ga.: U.S. EPA.
- Hulskotte, J. H. J., Denier van der Gon, H. A. C., Visschedijk, A. J. H., & Schaap, M. (2007). Brake wear from vehicles as an important source of diffuse copper pollution. *Water Science & Technology*, 56(1), 223-231.
- Huston, R., Chan, Y. C., Gardner, T., Shaw, G., & Chapman, H. (2009). Characterisation of atmospheric deposition as a source of contaminants in urban rainwater tanks. *Water Research*, 43(6), 1630-1640, doi:10.1016/j.watres.2008.12.045.
- Irish, L. B., Barrett, M. E., Malina, J. F., & Charbeneau, R. J. (1998). Use of regression models for analyzing highway storm-water loads. *Journal of Environmental Engineering*, 124(10), 987-993.
- James, W., & Shahin, R. (1998). A laboratory examination of pollutants leached from four different pavements by acid rain. In W. James (Ed.), *Advances in Modeling the Management of Stormwater Impacts* (Vol. 6). Ontario, Canada: Computational Hydraulics International.
- James, W., & von Langsdorff, H. (2003). *The use of permeable concrete block pavement in controlling environmental stressors in urban areas*. Paper presented at the Proceedings of the 7th International Conference on Concrete Block Paving (PAVE AFRICA 2003), South Africa, 2003.
- Jewell, T. K., & Adrian, D. D. (1982). Statistical analysis to derive improved stormwater quality models. *Journal of the Water Pollution Control Federation*, 54(5), 489-499.
- John, V. M. (2003). On the sustainability of concrete. *UNEP Industry and Environment*, 62-63.
- Kaiser, H. (1974). An index of factorial simplicity. *Psychometrika*, 39(1), 31-36, doi:10.1007/bf02291575.
- Kaiser, H. F. (1960). The application of electronic computers to factor analysis. *Educational and Psychological Measurement*, 20(1), 141-151, doi:10.1177/001316446002000116.

- Kanazu, T., Matsumura, T., Nishiuchi, T., & Yamamoto, T. (2001). Effect of simulated acid rain on deterioration of concrete. *Water, air, and soil pollution*, 130(1-4), 1481-1486, doi:10.1023/a:1013925316797.
- Kanta Rao, V., Rao, M., Kumar, S., & Pokhriyal, S. (2006). Structural evaluation of cement concrete roads in Mumbai City. *Journal of Performance of Constructed Facilities*, 20(2), 156-166, doi:doi:10.1061/(ASCE)0887-3828(2006)20:2(156).
- Karlén, C., Odnevall Wallinder, I., Heijerick, D., & Leygraf, C. (2002). Runoff rates, chemical speciation and bioavailability of copper released from naturally patinated copper. *Environmental Pollution*, 120(3), 691-700, doi:10.1016/s0269-7491(02)00179-3.
- Karlén, C., Odnevall Wallinder, I., Heijerick, D., Leygraf, C., & Janssen, C. R. (2001). Runoff rates and ecotoxicity of zinc induced by atmospheric corrosion. *Science of the Total Environment*, 277(1-3), 169-180, doi:10.1016/s0048-9697(00)00872-x.
- Kaya, G., & Tuncel, G. (1997). Trace element and major ion composition of wet and dry deposition in Ankara, Turkey. *Atmospheric Environment*, 31(23), 3985-3998, doi:[http://dx.doi.org/10.1016/S1352-2310\(97\)00221-5](http://dx.doi.org/10.1016/S1352-2310(97)00221-5).
- Kayhanian, M., Singh, A., Suverkropp, C., & Borroum, S. (2003). Impact of annual average daily traffic on highway runoff pollutant concentrations. *Journal of Environmental Engineering*, 129(11), 975-990, doi:doi:10.1061/(ASCE)0733-9372(2003)129:11(975).
- Kayhanian, M., Suverkropp, C., Ruby, A., & Tsay, K. (2007). Characterization and prediction of highway runoff constituent event mean concentration. *Journal of Environmental Management*, 85(2), 279-295, doi:10.1016/j.jenvman.2006.09.024.
- Kennedy, P., & Gadd, J. (2000). Preliminary examination of trace elements in tyres, brake pads and road bitumen in New Zealand. Ministry of Transport.
- Kennedy, P., & Gadd, J. (2003). Evaluation of road surface contaminant loadings in Waitakere City for development of the Vehicle Fleet Emission Model-Water. Wellington: Ministry of Transport.
- Khan, S., Lau, S., Kayhanian, M., & Stenstrom, M. (2006). Oil and grease measurement in highway runoff - sampling time and event mean concentrations. *Journal of Environmental Engineering*, 132(3), 415-422, doi:doi:10.1061/(ASCE)0733-9372(2006)132:3(415).
- Kossmann, M., & Sturman, A. (2004). The surface wind field during winter smog nights in Christchurch and coastal Canterbury, New Zealand. *International Journal of Climatology*, 24(1), 93-108, doi:10.1002/joc.981.
- Kuznetsova, A., Brockhoff, P. B., & Christensen, R. H. B. (2014). lmerTest: tests for random and fixed effects for linear mixed effect models (lmer objects of lme4 package). R package version 2.0-6.
- Lamprea, K., & Ruban, V. (2008). *Micro pollutants in atmospheric deposition, roof runoff and storm water runoff of a suburban Catchment in Nantes, France*. Paper presented at the 11th International Conference on Urban Drainage, Edinburgh, Scotland, 2008.
- Lamprea, K., & Ruban, V. (2011). Characterization of atmospheric deposition and runoff water in a small suburban catchment. *Environmental Technology*, 32(10), 1141-1149, doi:10.1080/09593330.2010.528045.



- Lavín, N., & Marín, E. (2001). Dry deposition characteristics of heavy metals in Europe. *Toxicological & Environmental Chemistry*, 79(3-4), 127-136, doi:10.1080/02772240109358983.
- Lee, B.-K., & Park, G.-H. (2010). Characteristics of heavy metals in airborne particulate matter on misty and clear days. *Journal of Hazardous Materials*, 184(1-3), 406-416, doi:<http://dx.doi.org/10.1016/j.jhazmat.2010.08.050>.
- Lee, J. H., & Bang, K. W. (2000). Characterization of urban stormwater runoff. *Water Research*, 34(6), 1773-1780, doi:10.1016/s0043-1354(99)00325-5.
- Legates, D. R., & McCabe, G. J. (1999). Evaluating the use of 'goodness-of-fit' measures in hydrologic and hydroclimatic model validation. *Water Resource Research*, 35(1), 233-241, doi:10.1029/1998WR900018.
- Legret, M., Colandini, V., & Le Marc, C. (1996). Effects of a porous pavement with reservoir structure on the quality of runoff water and soil. *Science of the Total Environment*, 189-190, 335-335, doi:10.1016/0048-9697(96)05228-x.
- Legret, M., Odie, L., Demare, D., & Jullien, A. (2005). Leaching of heavy metals and polycyclic aromatic hydrocarbons from reclaimed asphalt pavement. *Water Research*, 39(15), 3675-3685, doi:<http://dx.doi.org/10.1016/j.watres.2005.06.017>.
- Lenschow, P., Abraham, H. J., Kutzner, K., Lutz, M., Preuß, J. D., & Reichenbacher, W. (2001). Some ideas about the sources of PM<sub>10</sub>. *Atmospheric Environment*, 35, Supplement 1(0), S23-S33, doi:[http://dx.doi.org/10.1016/S1352-2310\(01\)00122-4](http://dx.doi.org/10.1016/S1352-2310(01)00122-4).
- Li, H., Qian, X., & Wang, Q. (2013). Heavy metals in atmospheric particulate matter: A comprehensive understanding is needed for monitoring and risk mitigation. *Environmental Science & Technology*, 47(23), 13210-13211, doi:10.1021/es404751a.
- Lim, J.-H., Sabin, L. D., Schiff, K. C., & Stolzenbach, K. D. (2006). Concentration, size distribution, and dry deposition rate of particle-associated metals in the Los Angeles region. *Atmospheric Environment*, 40, 7810-7823, doi:<http://dx.doi.org/10.1016/j.atmosenv.2006.07.025>.
- Lin, J.-M., Fang, G.-C., Holsen, T. M., & Noll, K. E. (1993). A comparison of dry deposition modeled from size distribution data and measured with a smooth surface for total particle mass, lead and calcium in Chicago. *Atmospheric Environment. Part A. General Topics*, 27(7), 1131-1138, doi:10.1016/0960-1686(93)90148-r.
- Lindberg, S., & Harriss, R. (1981). The role of atmospheric deposition in an eastern U.S. deciduous forest. *Water, air, and soil pollution*, 16(1), 13-31, doi:10.1007/bf01047039.
- Lindberg, S. E. (1982). Factors influencing trace metal, sulfate and hydrogen ion concentrations in rain. *Atmospheric Environment* (1967), 16(7), 1701-1709, doi:[http://dx.doi.org/10.1016/0004-6981\(82\)90263-3](http://dx.doi.org/10.1016/0004-6981(82)90263-3).
- Lindgren, Å. (1996). Asphalt wear and pollution transport. *Science of the Total Environment*, 189-190(0), 281-286, doi:[http://dx.doi.org/10.1016/0048-9697\(96\)05220-5](http://dx.doi.org/10.1016/0048-9697(96)05220-5).
- Lindh, G. (1972). Urbanization: a hydrological headache. *Ambio*, 1(6), 185-201.
- Lindner-Lunsford, J. B., & Ellis, S. R. (1987). Comparison of conceptually based and regression rainfall-runoff models, Denver metropolitan area, Colorado, and potential applications in urban areas. *Water-Resources Investigations Report 87-4104*: U.S. Geological Survey.
- Lindstrom, D., & Wallinder, I. O. (2011). Long-term use of galvanized steel in external applications. Aspects of patina formation, zinc runoff, barrier properties of surface

- treatments, and coatings and environmental fate. *Environmental Monitoring and Assessment*, 173(1-4), 139-153, doi:10.1007/s10661-010-1377-8.
- Liu, A., Egodawatta, P., & Goonetilleke, A. (2011). *Variability of input parameters related to pollutants build-up in stormwater quality modelling*. Paper presented at the Proceedings of 34th IAHR World Congress, Brisbane, Queensland, 2011.
- Liu, A., Egodawatta, P., Guan, Y., & Goonetilleke, A. (2013). Influence of rainfall and catchment characteristics on urban stormwater quality. *Science of the Total Environment*, 444, 255-262, doi:<http://dx.doi.org/10.1016/j.scitotenv.2012.11.053>.
- Lu, R., Turco, R. P., Stolzenbach, K., Friedlander, S. K., Xiong, C., Schiff, K., et al. (2003). Dry deposition of airborne trace metals on the Los Angeles Basin and adjacent coastal waters. *Journal of Geophysical Research: Atmospheres*, 108(D2), 4074, doi:10.1029/2001jd001446.
- Luhana, L., Sokhi, R., Warner, L., Mao, H., Boulter, P., McCrae, I., et al. (2004). Particulates characterisation of exhaust particulate emissions from road vehicles *Measurement of non-exhaust particulate matter*: European Commission: Directorate General Transport and Environment
- Lynam, M., Dvonch, J. T., Hall, N., Morishita, M., & Barres, J. (2014). Spatial patterns in wet and dry deposition of atmospheric mercury and trace elements in central Illinois, USA. *Environmental Science and Pollution Research*, 21(6), 4032-4043, doi:10.1007/s11356-013-2011-4.
- Manoli, E., Voutsas, D., & Samara, C. (2002). Chemical characterization and source identification/apportionment of fine and coarse air particles in Thessaloniki, Greece. *Atmospheric Environment*, 36(6), 949-961, doi:[http://dx.doi.org/10.1016/S1352-2310\(01\)00486-1](http://dx.doi.org/10.1016/S1352-2310(01)00486-1).
- Marx, S. K., Kamber, B. S., & McGowan, H. A. (2005a). Estimates of Australian dust flux into New Zealand: Quantifying the eastern Australian dust plume pathway using trace element calibrated  $^{210}\text{Pb}$  as a monitor. *Earth and Planetary Science Letters*, 239(3-4), 336-351, doi:<http://dx.doi.org/10.1016/j.epsl.2005.09.002>.
- Marx, S. K., Kamber, B. S., & McGowan, H. A. (2005b). Provenance of long-travelled dust determined with ultra-trace-element composition: a pilot study with samples from New Zealand glaciers. *Earth Surface Processes and Landforms*, 30(6), 699-716, doi:10.1002/esp.1169.
- Marx, S. K., Kamber, B. S., & McGowan, H. A. (2008). Scavenging of atmospheric trace metal pollutants by mineral dusts: Inter-regional transport of Australian trace metal pollution to New Zealand. *Atmospheric Environment*, 42(10), 2460-2478, doi:<http://dx.doi.org/10.1016/j.atmosenv.2007.12.014>.
- McPherson, T. N., Burian, S. J., Brown, M. J., Streit, G. E., & Turin, H. J. (2013). Integrated environmental modeling of the urban ecosystem. In *Earth Science in the City* (pp. 279-302): American Geophysical Union.
- Meyer, J. L., Paul, M. J., & Taulbee, W. K. (2005). Stream ecosystem function in urbanizing landscapes. *Journal of the North American Benthological Society*, 24(3), 602-612.
- Meyer, L. D., & Harmon, W. C. (1979). Multiple-intensity rainfall simulator for erosion research on row sideslopes. *Transactions of the ASAE*, 100-103.
- MfE (2011a). Clean healthy air for all New Zealanders: national air quality compliance strategy to meet the PM<sub>10</sub> standard. Wellington: Ministry for the Environment.

- MfE (2011b). Users' guide to the revised National Environmental Standards for Air Quality. Wellington: Ministry for the Environment.
- Mijić, Z., Stojić, A., Perišić, M., Rajšić, S., Tasić, M., Radenković, M., et al. (2010). Seasonal variability and source apportionment of metals in the atmospheric deposition in Belgrade. *Atmospheric Environment*, 44(30), 3630-3637, doi:<http://dx.doi.org/10.1016/j.atmosenv.2010.06.045>.
- Ministry for the Environment (2011). 2011 Users' Guide to the revised National Environmental Standards for Air Quality. Wellington: Ministry for the Environment.
- Ministry of Transport (2014). Infrastructure and investment. <http://www.transport.govt.nz/ourwork/tmif/infrastructureandinvestment/>. Accessed 16/09/2014.
- Moores, J., Pattinson, P., & Hyde, C. (2009). Enhancing the control of contaminants from New Zealand's roads: results of a road runoff sampling programme. *New Zealand Transport Agency research report 395*. Auckland: National Institute of Water and Atmospheric Research Ltd.
- Morselli, L., Cecchini, M., Grand, E., Iannuccilli, A., Barilli, L., & Olivieri, P. (1999). Heavy metals in atmospheric surrogate dry deposition. *Chemosphere*, 38(4), 899-907, doi:[http://dx.doi.org/10.1016/S0045-6535\(98\)00309-9](http://dx.doi.org/10.1016/S0045-6535(98)00309-9).
- Morselli, L., Olivieri, P., Brusori, B., & Passarini, F. (2003). Soluble and insoluble fractions of heavy metals in wet and dry atmospheric depositions in Bologna, Italy. *Environmental Pollution*, 124(3), 457-469, doi:[http://dx.doi.org/10.1016/S0269-7491\(03\)00013-7](http://dx.doi.org/10.1016/S0269-7491(03)00013-7).
- Motelay-Massei, A., Ollivon, D., Tiphagne, K., & Garban, B. (2005). Atmospheric bulk deposition of trace metals to the Seine River Basin, France: concentrations, sources and evolution from 1988 to 2001 in Paris. *Water, air, and soil pollution*, 164(1-4), 119-135, doi:10.1007/s11270-005-1659-x.
- Mourand, M., Bertrand-Krajewski, J. L., & Chebbo, G. (2005). Calibration and validation of multiple regression models for stormwater quality prediction: data partitioning, effect of dataset size and characteristics. *Water Science & Technology*, 52(3), 45-52.
- Muezzinoglu, A., & Cizmecioglu, S. C. (2006). Deposition of heavy metals in a Mediterranean climate area. *Atmospheric Research*, 81(1), 1-16, doi:<http://dx.doi.org/10.1016/j.atmosres.2005.10.004>.
- Mukhtar, A., & Limbeck, A. (2013). Recent developments in assessment of bio-accessible trace metal fractions in airborne particulate matter: A review. *Analytica Chimica Acta*, 774(0), 11-25, doi:<http://dx.doi.org/10.1016/j.aca.2013.02.008>.
- Nakagawa, S., & Schielzeth, H. (2013). A general and simple method for obtaining  $R^2$  from generalized linear mixed-effect models. *Methods in Ecology & Evolution*, 4, 133-142, doi:10.1111/j.2041-210x.2012.00261.x.
- NAPA & EAPA (2011). The asphalt paving industry: a global perspective. (2nd ed.). Brussels, Belgium and Maryland, U.S.: European Asphalt Pavement Association and National Asphalt Pavement Association.
- Nazahiyah, R., Yusop, Z., & Abustan, I. (2007). Stormwater quality and pollution loading from an urban residential catchment in Johor, Malaysia. *Water Science & Technology*, 56(7), 1-9, doi:10.2166/wst.2007.692.

- Neller, R. J. (1988). A comparison of channel erosion in small urban and rural catchments, Armidale, New South Wales. *Earth Surface Processes and Landforms*, 13(1), 1-7, doi:10.1002/esp.3290130102.
- Neville, A. M., & Brooks, J. J. (2010). *Concrete technology* (second ed.). Essex, England: Pearson Education Limited.
- New Zealand Government (2010). National infrastructure plan: March 2010. Ministry of Infrastructure.
- Nicholson, K. W. (1988). A review of particle resuspension. *Atmospheric Environment* (1967), 22(12), 2639-2651, doi:[http://dx.doi.org/10.1016/0004-6981\(88\)90433-7](http://dx.doi.org/10.1016/0004-6981(88)90433-7).
- Nicholson, K. W. (1993). Wind tunnel experiments on the resuspension of particulate material. *Atmospheric Environment. Part A. General Topics*, 27(2), 181-188, doi:[http://dx.doi.org/10.1016/0960-1686\(93\)90349-4](http://dx.doi.org/10.1016/0960-1686(93)90349-4).
- Nicholson, K. W., & Branson, J. R. (1990). Factors affecting resuspension by road traffic. *Science of the Total Environment*, 93(0), 349-358, doi:[http://dx.doi.org/10.1016/0048-9697\(90\)90126-F](http://dx.doi.org/10.1016/0048-9697(90)90126-F).
- NJDEP (2004). Computing stormwater runoff rates and volumes. In *New Jersey Stormwater Best Management Practices Manual*. New Jersey: New Jersey Department of Environmental Protection: Division of Watershed Management.
- Noll, K. E., Fang, K. Y. P., & Watkins, L. A. (1988). Characterization of the deposition of particles from the atmosphere to a flat plate. *Atmospheric Environment* (1967), 22(7), 1461-1468, doi:[http://dx.doi.org/10.1016/0004-6981\(88\)90170-9](http://dx.doi.org/10.1016/0004-6981(88)90170-9).
- NRRP (2009). Canterbury Natural Resources Regional Plan (2009). Environment Canterbury.
- NZ Transport Agency (2011). Specification for roading bitumens. (Vol. SPSM1: 2010 110114).
- O'Sullivan, A., Wicke, D., & Cochrane, T. (2012). Heavy metal contamination in an urban stream fed by contaminated air-conditioning and stormwater discharges. *Environmental Science and Pollution Research*, 19(3), 903-911, doi:10.1007/s11356-011-0639-5.
- Obropta, C. C., & Kardos, J. S. (2007). Review of urban stormwater quality models: Deterministic, stochastic, and hybrid approaches. *Journal of the American Water Resources Association*, 43(6), 1508-1523, doi:10.1111/j.1752-1688.2007.00124.x.
- Olejnik, S., & Algina, J. (2000). Measure of effect size for comparative studies: applications, interpretations, and limitations. *Contemporary Educational Psychology*, 25, 241-286.
- Onasch, T. B., Jayne, J. T., Herndon, S., Worsnop, D. R., Miake-Lye, R. C., Mortimer, I. P., et al. (2009). Chemical properties of aircraft engine particulate exhaust emissions. *Journal of Propulsion and Power*, 25(5), 1121-1137, doi:10.2514/1.36371.
- Opher, T., & Friedler, E. (2009). A preliminary coupled MT-GA model for the prediction of highway runoff quality. *Science of the Total Environment*, 407(15), 4490-4496, doi:<http://dx.doi.org/10.1016/j.scitotenv.2009.04.043>.
- Opher, T., & Friedler, E. (2010). Factors affecting highway runoff quality. *Urban Water Journal*, 7(3), 155-172, doi:10.1080/15730621003782339.
- Österle, W., Prietzel, C., Kloth, H., & Dmitriev, A. I. (2010). On the role of copper in brake friction materials. *Tribology International*, 43(12), 2317-2326, doi:<http://dx.doi.org/10.1016/j.triboint.2010.08.005>.

- Pagotto, C., Rémy, N., Legret, M., & Le Cloirec, P. (2001). Heavy metal pollution of road dust and roadside soil near a major rural highway. *Environmental Technology*, 22(3), 307-319, doi:10.1080/09593332208618280.
- Pandey, S., Taylor, M., & Lee, R. (2005). Reduction of road runoff contaminants: laboratory experiments and monitoring of treatment walls. In *Land Transport New Zealand Research Report 282* (Ed.), (Vol. 36pp). Wellington.
- Paode, R. D., Sofuoglu, S. C., Sivadechathep, J., Noll, K. E., Holsen, T. M., & Keeler, G. J. (1998). Dry deposition fluxes and mass size distributions of Pb, Cu, and Zn measured in Southern Lake Michigan during AEOLUS. *Environmental Science & Technology*, 32(11), 1629-1635, doi:10.1021/es970892b.
- Park, D., Jang, S., & Roesner, L. A. (2014). Evaluation of multi-use stormwater detention basins for improved urban watershed management. *Hydrological Processes*, 28(3), 1104-1113, doi:10.1002/hyp.9658.
- Parker, S. T., & Kinnersley, R. P. (2004). A computational and wind tunnel study of particle dry deposition in complex topography. *Atmospheric Environment*, 38(23), 3867-3878, doi:<http://dx.doi.org/10.1016/j.atmosenv.2004.03.046>.
- Patra, A., Colville, R., Arnold, S., Bowen, E., Shallcross, D., Martin, D., et al. (2008). On street observations of particulate matter movement and dispersion due to traffic on an urban road. *Atmospheric Environment*, 42(17), 3911-3926, doi:<http://dx.doi.org/10.1016/j.atmosenv.2006.10.070>.
- Paul, M. J., & Meyer, J. L. (2001). Streams in the urban landscape. *Annual Review of Ecology and Systematics*, 32, 333-365, doi:10.1146/annurev.ecolsys.32.081501.114040.
- Pennington, S. L., & Webster-Brown, J. G. (2008). Stormwater runoff quality from copper roofing, Auckland, New Zealand. *New Zealand Journal of Marine and Freshwater Research*, 42(1), 99-108, doi:10.1080/00288330809509940.
- Perkins, C., Nadim, F., & Arnold, W. R. (2005). Effects of PVC, cast iron and concrete conduit on concentrations of copper in stormwater. *Urban Water Journal*, 2(3), 183-191, doi:10.1080/15730620500236658.
- Pinheiro, J. C., & Bates, D. M. (2000). *Mixed-effects models in S and S-Plus*. New York: Springer-Verlag.
- Pitt, R., Field, R., Lalor, M., & Brown, M. (1995). Urban stormwater toxic pollutants: assessment, sources, and treatability. *Water Environment Research*, 67(3), 260-275, doi:10.2175/106143095X131466.
- Poissant, L., Schmit, J.-P., & Béron, P. (1994). Trace inorganic elements in rainfall in the Montreal Island. *Atmospheric Environment*, 28(2), 339-346, doi:[http://dx.doi.org/10.1016/1352-2310\(94\)90109-0](http://dx.doi.org/10.1016/1352-2310(94)90109-0).
- Polkowska, Ż., Górecki, T., & Namieśnik, J. (2011). Determination of atmospheric pollutants in wet deposition. *Environmental Reviews*, 19(1), 185-213, doi:10.1139/a11-006.
- Portland Cement Association and National Asphalt Pavement Association (1986). Asphalt vs. concrete. *American City & County*, 101(7), 30-38.
- Prestes, E. C., Anjos, V. E., Sodré, F. F., & Grassi, M. T. (2006). Copper, lead and cadmium loads and behavior in urban stormwater runoff in Curitiba, Brazil. *Journal of the Brazilian Chemical Society*, 17, 53-60, doi:<http://dx.doi.org/10.1590/S0103-50532006000100008>.



- R Core Team (2014). R: A language and environment for statistical computing. In R Foundation for Statistical Computing (Ed.). Vienna, Austria: <http://www.R-project.org/>.
- Radke, L. F., Hobbs, P. V., & Eltgroth, M. W. (1980). Scavenging of aerosol particles by precipitation. *Journal of Applied Meteorology*, 19(6), 715-722, doi:10.1175/1520-0450(1980)019<0715:soapbp>2.0.co;2.
- Rahn, K. A. (1981). The Mn/V ratio as a tracer of large-scale sources of pollution aerosol for the Arctic. *Atmospheric Environment* (1967), 15(8), 1457-1464, doi:[http://dx.doi.org/10.1016/0004-6981\(81\)90352-8](http://dx.doi.org/10.1016/0004-6981(81)90352-8).
- Ray, S., Khillare, P. S., & Kim, K. H. (2012). The effect of aircraft traffic emissions on the soil surface contamination analysis around the international airport in Delhi, India. *Asian Journal of Atmospheric Environment*, 6(2), 118-126.
- Rhodes, E. P., Ren, Z., & Mays, D. C. (2012). Zinc leaching from tire crumb rubber. *Environmental Science & Technology*, 46(23), 12856-12863, doi:10.1021/es3024379.
- RMA (1991). Resource Management Act 1991: Public Act 1991 No. 69.
- Roberts, F. L., Kandhal, P. S., Brown, E. R., Lee, D. Y., & Kennedy, T. W. (1996). *Hot mix asphalt materials, mixture design, and construction*. Maryland, U.S.A.: NAPA Educational Foundation.
- Robien, A., Striebel, T., & Herrmann, R. (1997). Modeling of dissolved and particle-bound pollutants in urban street runoff. *Wat. Sci. Tech.*, 36(8-9), 77-82.
- Rocher, V., Azimi, S., Gasperi, J., Beuvin, L., Muller, M., Moilleron, R., et al. (2004). Hydrocarbons and metals in atmospheric deposition and roof runoff in Central Paris. *Water, air, and soil pollution*, 159, 67-86, doi:10.1023/b:wate.0000049165.12410.98.
- Rogge, W. F., Hildemann, L. M., Mazurek, M. A., Cass, G. R., & Simoneit, B. R. T. (1993). Sources of fine organic aerosol. 3. Road dust, tire debris, and organometallic brake lining dust: roads as sources and sinks. *Environmental Science & Technology*, 27(9), 1892-1904, doi:10.1021/es00046a019.
- Roy, J. W., & Bickerton, G. (2011). Toxic groundwater contaminants: an overlooked contributor to urban stream syndrome? *Environmental Science & Technology*, 46(2), 729-736, doi:10.1021/es2034137.
- Rubio, M. C., Martínez, G., Baena, L., & Moreno, F. (2012). Warm mix asphalt: an overview. *Journal of Cleaner Production*, 24, 76-84, doi:<http://dx.doi.org/10.1016/j.jclepro.2011.11.053>.
- Ruellan, S., & Cachier, H. (2001). Characterisation of fresh particulate vehicular exhausts near a Paris high flow road. *Atmospheric Environment*, 35(2), 453-468, doi:[http://dx.doi.org/10.1016/S1352-2310\(00\)00110-2](http://dx.doi.org/10.1016/S1352-2310(00)00110-2).
- Rushton, B. (2001). Low-impact parking lot design reduces runoff and pollutant loads. *Journal of Water Resources Planning and Management*, 127(3), 172-179, doi:doi:10.1061/(ASCE)0733-9496(2001)127:3(172).
- Ryan, P. A. (1991). Environmental effects of sediment on New Zealand streams: A review. *New Zealand Journal of Marine and Freshwater Research*, 25(2), 207-221, doi:10.1080/00288330.1991.9516472.
- Sabin, L. D., Lim, J. H., Stolzenbach, K. D., & Schiff, K. C. (2005). Contribution of trace metals from atmospheric deposition to stormwater runoff in a small impervious urban catchment. *Water Research*, 39(16), 3929-3937, doi:10.1016/j.watres.2005.07.003.

- Sabin, L. D., Lim, J. H., Stolzenbach, K. D., & Schiff, K. C. (2006). Atmospheric dry deposition of trace metals in the coastal region of Los Angeles, California, USA. *Environmental Toxicology and Chemistry*, 25(9), 2334-2341, doi:10.1897/05-300R.1.
- Sadler, R., Delamont, C., White, P., & Connell, D. (1999). Contaminants in soil as a result of leaching from asphalt. *Toxicological & Environmental Chemistry*, 68(1-2), 71-81, doi:10.1080/02772249909358646.
- Salomon, V. (2014). Air quality status report PM<sub>2.5</sub>. Christchurch, New Zealand: Environment Canterbury.
- Sansalone, J., Kuang, X., & Ranieri, V. (2008). Permeable pavement as a hydraulic and filtration interface for urban drainage. *Journal of Irrigation and Drainage Engineering*, 134(5), 666-674, doi:10.1061/(ASCE)0733-9437(2008)134:5(666).
- Sansalone, J., & Ying, G. (2008). Partitioning and granulometric distribution of metal leachate from urban traffic dry deposition particulate matter subject to acidic rainfall and runoff retention. *Water Research*, 42(15), 4146-4162.
- Sansalone, J. J., & Buchberger, S. G. (1997). Partitioning and first flush of metals in urban roadway storm water. *Journal of Environmental Engineering*, 123(2), 134-143.
- Santero, N., Loijos, A., & Ochsendorf, J. (2013). Greenhouse gas emissions reduction opportunities for concrete pavements. *Journal of Industrial Ecology*, 17(6), 859-868, doi:10.1111/jiec.12053.
- Sartor, J. D., & Boyd, G. B. (1972). Water pollution aspects of street surface contaminants Washington, D.C.: Office of Research and Monitoring U.S. Environmental Protection Agency.
- Sartor, J. D., Boyd, G. B., & Agardy, F. J. (1974). Water pollution aspects of street surface contaminants. *Journal (Water Pollution Control Federation)*, 46(3), 458-467.
- Scholz, M., & Grabowiecki, P. (2007). Review of permeable pavement systems. *Building and Environment*, 42(11), 3830-3836, doi:10.1016/j.buildenv.2006.11.016.
- Scott, A. J. (2005). *Source apportionment and chemical characterisation of airborne fine particulate matter in Christchurch, New Zealand*. University of Canterbury, Christchurch.
- Scott, A. J., & Sturman, A. P. (2006). Beyond emission inventories: Tracking the main sources of airborne PM in Christchurch, New Zealand. *Clean Air and Environmental Quality*, 40(4), 35-42.
- Seaburn, G. E. (1969). Effects of urban development on direct runoff to East Meadow Brook, Nassau County, Long Island, New York. *Geological Survey Professional Paper 627-B*: Geological Survey Professional Paper 627-B.
- Sehmel, G. A. (1973). Particle resuspension from an asphalt road caused by car and truck traffic. *Atmospheric Environment* (1967), 7(3), 291-309, doi:[http://dx.doi.org/10.1016/0004-6981\(73\)90078-4](http://dx.doi.org/10.1016/0004-6981(73)90078-4).
- Sehmel, G. A. (1980a). Particle and gas dry deposition: A review. *Atmospheric Environment* (1967), 14(9), 983-1011, doi:[http://dx.doi.org/10.1016/0004-6981\(80\)90031-1](http://dx.doi.org/10.1016/0004-6981(80)90031-1).
- Sehmel, G. A. (1980b). Particle resuspension: A review. *Environment International*, 4(2), 107-127, doi:[http://dx.doi.org/10.1016/0160-4120\(80\)90005-7](http://dx.doi.org/10.1016/0160-4120(80)90005-7).
- Seinfeld, J. H., & Pandis, S. N. (2006). *Atmospheric chemistry and physics: from air pollution to climate change* (2nd edition ed.). New Jersey: John Wiley & Sons, Inc.

- Shah, M., Shaheen, N., & Jaffar, M. (2006). Characterization, source identification and apportionment of selected metals in TSP in an urban atmosphere. *Environmental Monitoring and Assessment*, 114(1-3), 573-587, doi:10.1007/s10661-006-4940-6.
- Shaheen, D. G. (1975). Contributions of urban roadway usage to water pollution. (Vol. 600/2-75-004). Washington D.C., U.S.A.: U.S. Environmental Protection Agency.
- Shammaa, Y., Zhu, D. Z., Gyürek, L. L., & Labatiuk, C. W. (2002). Effectiveness of dry ponds for stormwater total suspended solids removal. *Canadian Journal of Civil Engineering*, 29(2), 316-324, doi:10.1139/102-008.
- Shrivastav, R. (2001). Atmospheric heavy metal pollution. *Resonance*, 6(4), 62-68, doi:10.1007/bf02994594.
- Shu, X., Huang, B., Wu, H., Dong, Q., & Burdette, E. G. (2011). Performance comparison of laboratory and field produced pervious concrete mixtures. *Construction and Building Materials*, 25(8), 3187-3192, doi:<http://dx.doi.org/10.1016/j.conbuildmat.2011.03.002>.
- Smithson, J. (2011). Inventory of emissions to air in Christchurch, 2009. Christchurch: Environment Canterbury.
- Smolders, E., & Degryse, F. (2002). Fate and effect of zinc from tire debris in soil. *Environmental Science & Technology*, 36(17), 3706-3710, doi:10.1021/es025567p.
- Soonthornnonda, P., & Christensen, E. R. (2005). MMSD stormwater monitoring program data analysis 2004-2005, final report. Milwaukee, Wisconsin: University of Wisconsin-Milwaukee.
- Spronken-Smith, R. A., Sturman, A. P., & Wilton, E. V. (2002). The air pollution problem in Christchurch, New Zealand - progress and prospects. *Clean Air and Environmental Quality*, 36(1), 23-28.
- Sternbeck, J., Sjödin, Å., & Andréasson, K. (2002). Metal emissions from road traffic and the influence of resuspension—results from two tunnel studies. *Atmospheric Environment*, 36(30), 4735-4744, doi:10.1016/s1352-2310(02)00561-7.
- Stotz, G., & Krauth, K. (1994). Pollution of effluents from pervious pavements of an experimental highway section. First results. *Science of the Total Environment*, 146-47, 465-465, doi:10.1016/0048-9697(94)90270-4.
- Stroombergen, A. (2013). The case for concrete roads: for Cement and Concrete Association of New Zealand. Infometrics Ltd.
- Stull, R. B. (1995). *Meteorology today for scientists and engineers*. Minneapolis: West Publishing Company.
- Sturman, A., Titov, M., & Zawar-Reza, P. (2011). Selecting optimal monitoring site locations for peak ambient particulate material concentrations using the MM5-CAMx4 numerical modelling system. *Science of the Total Environment*, 409(4), 810-821, doi:10.1016/j.scitotenv.2010.11.005.
- Sturman, A. P. (1985). An examination of the role of local wind systems in the concentration and dispersion of smoke pollution in Christchurch, New Zealand. *New Zealand Geographer*, 41(2), 67-76, doi:10.1111/j.1745-7939.1985.tb01073.x.
- Sundberg, R. (1998). The fate of copper released from the Vasa Ship Museum. *Metall*, 52(4), 230-231.
- Suren, A. M. (2000). Effects of urbanisation. In K. J. Collier, & M. J. Winterbourn (Eds.), *New Zealand Stream Invertebrates: Ecology and Implications for Management* (pp. 260-288). Hamilton: New Zealand Limnological Society.



- Sutherland, R. A., & Tolosa, C. A. (2001). Variation in total and extractable elements with distance from roads in an urban watershed, Honolulu, Hawaii. *Water, Air, & Soil Pollution*, 127(1), 315-338, doi:10.1023/a:1005283932003.
- Takeda, K., Marumoto, K., Minamikawa, T., Sakugawa, H., & Fujiwara, K. (2000). Three-year determination of trace metals and the lead isotope ratio in rain and snow depositions collected in Higashi-Hiroshima, Japan. *Atmospheric Environment*, 34(26), 4525-4535, doi:[http://dx.doi.org/10.1016/S1352-2310\(00\)00103-5](http://dx.doi.org/10.1016/S1352-2310(00)00103-5).
- Tanner, P. A., & Wong, A. Y. S. (2000). Soluble trace metals and major ionic species in the bulk deposition and atmosphere of Hong Kong. *Water, air, and soil pollution*, 122(3-4), 261-279, doi:10.1023/a:1005232313641.
- Tecer, L. H., Süren, P., Alagha, O., Karaca, F., & Tuncel, G. (2008). Effect of meteorological parameters on fine and coarse particulate matter mass concentration in a coal-mining area in Zonguldak, Turkey. *Journal of the Air & Waste Management Association*, 58(4), 543-552.
- Thamer, M., Rupak, A., Saravanamuthu, V., & Paripurnanda, L. (2012). Removal of heavy metals in stormwater by hydrous ferric oxide. *Proceedings of the Institution of Civil Engineers. Water management*, 165(3), 171.
- Tippayawong, N., Pengchai, P., & Lee, A. (2006). Characterization of ambient aerosols in Northern Thailand and their probable sources. *Int. J. Environ. Sci. Tech.*, 3(4), 359-369.
- Transit New Zealand (2007). New Zealand supplement to the document, pavement design - a guide to the structural design of road pavements (AUSTROADS, 2004). (Vol. 2).
- U.S. EPA (2009). National Pollutant Discharge Elimination System (NPDES). <http://cfpub.epa.gov/npdes/>. Accessed 08/04/2014.
- US EPA (2008). Lead emissions from the use of leaded aviation gasoline in the United States. *Technical support document EPA420-R-08-020*.
- Vardoulakis, S., Fisher, B. E. A., Pericleous, K., & Gonzalez-Flesca, N. (2003). Modelling air quality in street canyons: a review. *Atmospheric Environment*, 37(2), 155-182, doi:[http://dx.doi.org/10.1016/S1352-2310\(02\)00857-9](http://dx.doi.org/10.1016/S1352-2310(02)00857-9).
- Vaze, J., & Chiew, F. H. S. (2002). Experimental study of pollutant accumulation on an urban road surface. *Urban Water*, 4(4), 379-389, doi:[http://dx.doi.org/10.1016/S1462-0758\(02\)00027-4](http://dx.doi.org/10.1016/S1462-0758(02)00027-4).
- Vaze, J., & Chiew, F. H. S. (2003a). Comparative evaluation of urban storm water quality models. *Water Resources Research*, 39(10), 1280, doi:10.1029/2002wr001788.
- Vaze, J., & Chiew, F. H. S. (2003b). Study of pollutant washoff from small impervious experimental plots. *Water Resource Research*, 39(6), 1160, doi:10.1029/2002wr001786.
- Vollertsen, J., Lange, K. H., Pedersen, J., & Hallager, P. (2009). Monitoring the startup of a wet detention pond equipped with sand filters and sorption filters. *Water Science & Technology*, 60(4), 1071-1079, doi:10.2166/wst.2009.460.
- Waara, S., & Färm, C. (2008). An assessment of the potential toxicity of runoff from an urban roadscape during rain events. *Environmental Science and Pollution Research*, 15(3), 205-210, doi:10.1065/espr2007.12.463.
- Walsh, C. J., Allison, H. R., Feminella, J. W., Cottingham, P. D., Groffman, P. M., & Ii, R. P. M. (2005). The urban stream syndrome: current knowledge and the search for a cure. *Journal of the North American Benthological Society*, 24(3), 706-723.

- Wang, L., Lyons, J., & Kanehl, P. (2003). Impacts of urbanization on stream habitat and fish across multiple scales. *Environmental Management*, 28(2), 255-266.
- Wang, L., Wei, J., Huang, Y., Wang, G., & Madqsood, I. (2011). Urban nonpoint source pollution buildup and washoff models for simulating storm runoff quality in the Los Angeles County. *Environmental Pollution*, 159, 1932-1940.
- Wang, S., He, Q., Ai, H., Wang, Z., & Zhang, Q. (2013). Pollutant concentrations and pollution loads in stormwater runoff from different land uses in Chongqing. *Journal of Environmental Sciences*, 25(3), 502-510, doi:[http://dx.doi.org/10.1016/S1001-0742\(11\)61032-2](http://dx.doi.org/10.1016/S1001-0742(11)61032-2).
- Whiteoak, D. (1990). *The Shell bitumen handbook*. Surrey, U.K.: Shell Bitumen U.K.
- Whiting, E., & Clifford, H. (1983). Invertebrates and urban runoff in a small northern stream, Edmonton, Alberta, Canada. *Hydrobiologia*, 102(1), 73-80, doi:10.1007/bf00006052.
- WHO (2006). Air quality guidelines - global update. 2005. Particulate matter, ozone, nitrogen dioxide and sulfur dioxide. Copenhagen: World Health Organization Regional Office for Europe.
- Wicke, D., Cochrane, T. A., O' Sullivan, A. D., Cave, S., & Derksen, M. (2014). Effect of age and rainfall pH on contaminant yields from metal roofs. *Water Science & Technology*, 69(10), 2166-2173, doi:10.2166/wst.2014.124.
- Wicke, D., Cochrane, T. A., & O'Sullivan, A. (2012a). Build-up dynamics of heavy metals deposited on impermeable urban surfaces. *Journal of Environmental Management*, 113, 347-354, doi:10.1016/j.jenvman.2012.09.005.
- Wicke, D., Cochrane, T. A., & O'Sullivan, A. D. (2012b). Atmospheric deposition and storm induced runoff of heavy metals from different impermeable urban surfaces. *Journal of Environmental Monitoring*, 14(1), 209-216, doi:10.1039/c1em10643k.
- Wicke, D., Cochrane, T. A., & O'Sullivan, A. D. (2010). *An innovative method for spatial quantification of contaminant buildup and wash-off from impermeable urban surfaces*. Paper presented at the IWA World Water Congress and Exhibition (IWA 2010), Montreal, Canada, 19-24 Sept 2010.
- Wilson, J. G., Kingham, S., & Sturman, A. P. (2006). Intraurban variations of PM<sub>10</sub> air pollution in Christchurch, New Zealand: Implications for epidemiological studies. *Science of the Total Environment*, 367(2-3), 559-572, doi:<http://dx.doi.org/10.1016/j.scitotenv.2005.08.045>.
- Wilson, P. C. (2010). Water quality notes: alkalinity and hardness. SL332: Institute of Food and Agricultural Sciences, University of Florida.
- Wolman, M. G. (1967). A cycle of sedimentation and erosion in urban river channels. *Geografiska Annaler. Series A, Physical Geography*, 49(2/4), 385-395, doi:10.2307/520904.
- Wong, C. S. C., Li, X. D., Zhang, G., Qi, S. H., & Peng, X. Z. (2003). Atmospheric deposition of heavy metals in the Pearl River Delta, China. *Atmospheric Environment*, 37(6), 767-776, doi:10.1016/s1352-2310(02)00929-9.
- Wooten, R. D. (2011). Statistical analysis of the relationship between wind speed, pressure and temperature. *Journal of Applied Sciences*, 11(15), 2712-2722, doi:10.3923/jas.2011.2712.2722.
- Yaziz, M. I., Gunting, H., Sapari, N., & Ghazali, A. W. (1989). Variations in rainwater quality from roof catchments. *Water Research*, 23(6), 761-765, doi:[http://dx.doi.org/10.1016/0043-1354\(89\)90211-X](http://dx.doi.org/10.1016/0043-1354(89)90211-X).

- Zanders, J. M. (2005). Road sediment: characterization and implications for the performance of vegetated strips for treating road run-off. *Science of the Total Environment*, 339, 41-47, doi:10.1016/j.scitotenv.2004.07.023.
- Zaniewski, J. P. (1989). Effect of pavement surface type on fuel combustion. *Report no. SR289.01P*. Illinois, U.S.: Portland Cement Association.
- Zhang, L., & Vet, R. (2006). A review of current knowledge concerning size-dependent aerosol removal. *China Particuology*, 4(6), 272-282, doi:10.1016/s1672-2515(07)60276-0.
- Zhao, H., Li, X., Wang, X., & Tian, D. (2010). Grain size distribution of road-deposited sediment and its contribution to heavy metal pollution in urban runoff in Beijing, China. *Journal of Hazardous Materials*, 183(1-3), 203-210, doi:<http://dx.doi.org/10.1016/j.jhazmat.2010.07.012>.
- Ziegler, A. C. (2002). *Issues related to the use of turbidity measurements as a surrogate for suspended sediment*. Paper presented at the Turbidity and Other Sediment Surrogates Workshop, Reno, NV, April 30 - May 2.
- Zoppou, C. (2001). Review of urban storm water models. *Environmental Modelling & Software*, 16(3), 195-231, doi:[http://dx.doi.org/10.1016/S1364-8152\(00\)00084-0](http://dx.doi.org/10.1016/S1364-8152(00)00084-0).

# Appendices

## Appendix A - Process-Based Models

To examine the suitability of process-based models for predicting stormwater quality, pollutant build-up and wash-off functions were developed (as discussed in Section 6.3.2). The pollutant build-up and wash-off functions (eq. 6-1 & 6-2) were obtained from Egodawatta et al. (2009) “Understanding the Physical Processes of Pollutant Build-up and Wash-off on Roof Surfaces.”

$$B = aD^b \quad \text{eq. 6-1}$$

$$F_w = W/W_0 = C_f(1 - e^{-kIt}) \quad \text{eq. 6-2}$$

Where B = build-up load (mg/m<sup>2</sup>); a, b = empirical coefficients; D = number of dry days; F<sub>w</sub> = fraction wash-off; W = weight of the pollutant mobilised after time t; W<sub>0</sub> = initial weight of pollutant; C<sub>f</sub> = capacity factor; k = wash-off coefficient; I = rainfall intensity (mm/h); t = time (h).

The equations can be calibrated to different conditions (pavement type, land-use etc.) by varying the coefficients in the model. Therefore, for each land-use areas studied here, different coefficients had to be derived. However, as the methodology in this research did not allow for F<sub>w</sub> to be measured, nor could build-up load be measured, two major assumptions had to be made for coefficient derivation:

- (1) Any rainfall event that had a peak rainfall intensity greater than 5 mm/h and a rain depth greater than 20 mm was sufficient at removing all the pollutant build-up,
- (2) The initial weight of pollutants on a surface equaled the weight of pollutants washed-off during a rain event (W<sub>0</sub> = W) when the rain event that had a peak rainfall intensity greater than 5 mm/h and a rain depth greater than 20 mm.

Therefore, equations 5-1 and 5-2 were modified to:

$$\text{Runoff load} = aD^b \quad \text{eq. 6-3}$$

$$F_w = 1 = C_f(1 - e^{-kIt}) \quad \text{eq. 6-4}$$

The coefficients  $a$ ,  $b$ ,  $C_f$ , and  $k$  were determined using the least sum of the squared difference between modelled and experimental results using EXCEL Solver.

**Table A-1 results from the process-based models.**

	<b>Coefficients</b>	<b>Total Cu</b>	<b>Total Zn</b>	<b>Total Pb</b>	<b>TSS</b>
<i>Industrial</i>	$a$	116.284	1420.559	116.110	1049.871
	$b$	0.190	0	0.170	0
	$C_f$	106.303	1421.559	138.173	1050.871
	$k$	>0.3	>0.3	>0.3	>0.3
<i>Residential</i>	$a$	42.524	219.161	24.157	123.020
	$b$	0.446	0.543	0	0
	$C_f$	84.949	511.533	25.157	124.020
	$k$	>0.3	>0.3	>0.3	>0.3
<i>Airside</i>	$a$	2.181	3.304	1.617	2.808
	$b$	2.401	3.819	1.721	3.543
	$C_f$	31.481	220.422	11.706	138.622
	$k$	>0.3	>0.3	>0.3	>0.3

The results for the coefficients in the model (Table A-1) suggest that the assumption used to derive these values may be inaccurate, and therefore, the model itself is accurate. Firstly, in four instances, the  $b$  coefficient equaled zero, this implies that regardless of the number of antecedent dry days, pollutant build-up is the same. As antecedent dry days is known to have an influence on pollutant build-up (Opher et al. 2010), this results is invalid. Secondly, determining a correct value for the  $k$  coefficient was not possible. Any value which  $k > 0.3$  did not alter the value of the least sum of squares: as the  $-kIt$  term becomes large, the exponent value become negligible against the  $C_f$  term. Therefore, the assumption of total wash-off is inaccurate; this is not surprising as Vaze et al. (2003b) found that typical storms events could not remove the total pollutant load.

## Appendix B - Split Regression Models for Small and Large Rain Events

Two separate mixed effect models were developed for samples arising from small or large rain events. A small event was defined as a rain event with less than 5 mm of rainfall; a large event had over 5 mm of rainfall. The results of the models from the small events are represented in Table B-1; large events are represented in Table B-2. Splitting the data into small or large events did not add to the predictive performance of the models.

**Table B-1 Prediction models for pollutant runoff during a small rain event.**

		Model	R <sub>2</sub>
Ind	tCu	$\log(\text{Cu}) = 0.987 + 0.413 \cdot \text{atan}(\text{ADD}) + 0.571 \cdot \log(\text{RD})$	$R^2_{(m)} = 0.52, R^2_{(c)} = 0.53$
	tZn	$\log(\text{Zn}) = 1.775 + 0.204 \cdot \text{atan}(\text{ADD}) + 0.585 \cdot \log(\text{RD})$	$R^2_{(m)} = 0.21, R^2_{(c)} = 0.21$
	tPb	$\log(\text{Pb}) = 0.803 + 0.121 \cdot \text{atan}(\text{ADD}) + 0.326 \cdot \log(\text{Dur}) + 0.419 \cdot \log(\text{RI})$	$R^2_{(m)} = 0.10, R^2_{(c)} = 0.10$
	TSS	$\log(\text{TSS}) = 1.374 + 0.308 \cdot \text{atan}(\text{ADD}) + 0.430 \cdot \log(\text{Dur}) + 0.044 \cdot \log(\text{RI})$	$R^2_{(m)} = 0.25, R^2_{(c)} = 0.25$
Res	tCu	$\log(\text{Cu}) = 0.674 + 0.374 \cdot \text{atan}(\text{ADD}) + 0.333 \cdot \log(\text{RD})$	$R^2_{(m)} = 0.21, R^2_{(c)} = 0.21$
	tZn	$\log(\text{Zn}) = 1.304 + 0.182 \cdot \text{atan}(\text{ADD}) + 0.250 \cdot \log(\text{RD})$	$R^2_{(m)} = 0.05, R^2_{(c)} = 0.52$
	tPb	$\log(\text{Pb}) = 0.592 + 0.197 \cdot \text{atan}(\text{ADD}) - 0.328 \cdot \log(\text{Dur}) + 0.585 \cdot \log(\text{RI})$	$R^2_{(m)} = 0.23, R^2_{(c)} = 0.23$
	TSS	$\log(\text{TSS}) = 0.935 + 0.349 \cdot \text{atan}(\text{ADD}) + 0.213 \cdot \log(\text{Dur}) + 0.860 \cdot \log(\text{RI})$	$R^2_{(m)} = 0.55, R^2_{(c)} = 0.60$
Air	tCu	$\log(\text{Cu}) = 0.114 + 0.369 \cdot \text{atan}(\text{ADD}) + 1.353 \cdot \log(\text{RD})$	$R^2_{(m)} = 0.53, R^2_{(c)} = 0.53$
	tZn	$\log(\text{Zn}) = 1.108 + 0.040 \cdot \text{atan}(\text{ADD}) + 1.077 \cdot \log(\text{RD})$	$R^2_{(m)} = 0.23, R^2_{(c)} = 0.23$
	tPb	$\log(\text{Pb}) = -0.731 + 0.350 \cdot \text{atan}(\text{ADD}) + 0.933 \cdot \log(\text{Dur}) + 1.356 \cdot \log(\text{RI})$	$R^2_{(m)} = 0.41, R^2_{(c)} = 0.41$
	TSS	$\log(\text{TSS}) = 0.775 + 0.316 \cdot \text{atan}(\text{ADD}) + 0.612 \cdot \log(\text{Dur}) + 1.370 \cdot \log(\text{RI})$	$R^2_{(m)} = 0.54, R^2_{(c)} = 0.54$

**Table B-2 Prediction models for pollutant runoff during a small rain event.**

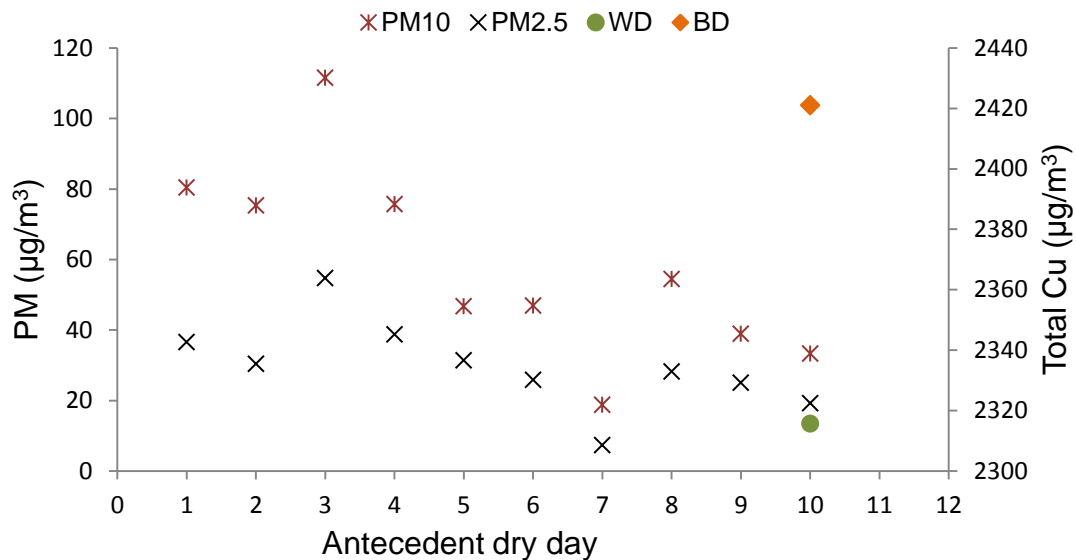
		<b>Model</b>	<b>R<sub>2</sub></b>
<i>Ind</i>	<i>tCu</i>	$\log(\text{Cu}) = 1.103 + 0.508 \cdot \text{atan}(\text{ADD}) + 0.223 \cdot \log(\text{RD})$	$R^2_{(m)} = 0.36, R^2_{(c)} = 0.36$
	<i>tZn</i>	$\log(\text{Zn}) = 1.541 + 0.551 \cdot \text{atan}(\text{ADD}) + 0.439 \cdot \log(\text{RD})$	$R^2_{(m)} = 0.42, R^2_{(c)} = 0.42$
	<i>tPb</i>	$\log(\text{Pb}) = 0.751 + 0.567 \cdot \text{atan}(\text{ADD}) - 0.047 \cdot \log(\text{Dur}) + 0.731 \cdot \log(\text{RI})$	$R^2_{(m)} = 0.58, R^2_{(c)} = 0.61$
	<i>TSS</i>	$\log(\text{TSS}) = 1.528 + 0.452 \cdot \text{atan}(\text{ADD}) + 0.219 \cdot \log(\text{Dur}) + 0.630 \cdot \log(\text{RI})$	$R^2_{(m)} = 0.59, R^2_{(c)} = 0.60$
<i>Res</i>	<i>tCu</i>	$\log(\text{Cu}) = 0.463 + 0.493 \cdot \text{atan}(\text{ADD}) + 0.429 \cdot \log(\text{RD})$	$R^2_{(m)} = 0.56, R^2_{(c)} = 0.56$
	<i>tZn</i>	$\log(\text{Zn}) = 1.035 + 0.236 \cdot \text{atan}(\text{AADD}) + 0.808 \cdot \log(\text{RD})$	$R^2_{(m)} = 0.50, R^2_{(c)} = 0.50$
	<i>tPb</i>	$\log(\text{Pb}) = 0.178 + 0.381 \cdot \text{atan}(\text{ADD}) + 0.147 \cdot \log(\text{Dur}) + 0.521 \cdot \log(\text{RI})$	$R^2_{(m)} = 0.48, R^2_{(c)} = 0.48$
	<i>TSS</i>	$\log(\text{TSS}) = 1.109 + 0.538 \cdot \text{atan}(\text{ADD}) + 0.097 \cdot \log(\text{Dur}) - 0.008 \cdot \log(\text{RI})$	$R^2_{(m)} = 0.62, R^2_{(c)} = 0.65$
<i>Air</i>	<i>tCu</i>	$\log(\text{Cu}) = 0.675 + 0.178 \cdot \text{atan}(\text{ADD}) + 0.600 \cdot \log(\text{RD})$	$R^2_{(m)} = 0.42, R^2_{(c)} = 0.42$
	<i>tZn</i>	$\log(\text{Zn}) = 1.195 + 0.207 \cdot \text{atan}(\text{ADD}) + 0.786 \cdot \log(\text{RD})$	$R^2_{(m)} = 0.38, R^2_{(c)} = 0.38$
	<i>tPb</i>	$\log(\text{Pb}) = -0.113 + 0.418 \cdot \text{atan}(\text{ADD}) + 0.245 \cdot \log(\text{Dur}) + 0.505 \cdot \log(\text{RI})$	$R^2_{(m)} = 0.53, R^2_{(c)} = 0.53$
	<i>TSS</i>	$\log(\text{TSS}) = 1.258 + 0.441 \cdot \text{atan}(\text{ADD}) + 0.160 \cdot \log(\text{Dur}) + 0.500 \cdot \log(\text{RI})$	$R^2_{(m)} = 0.36, R^2_{(c)} = 0.36$



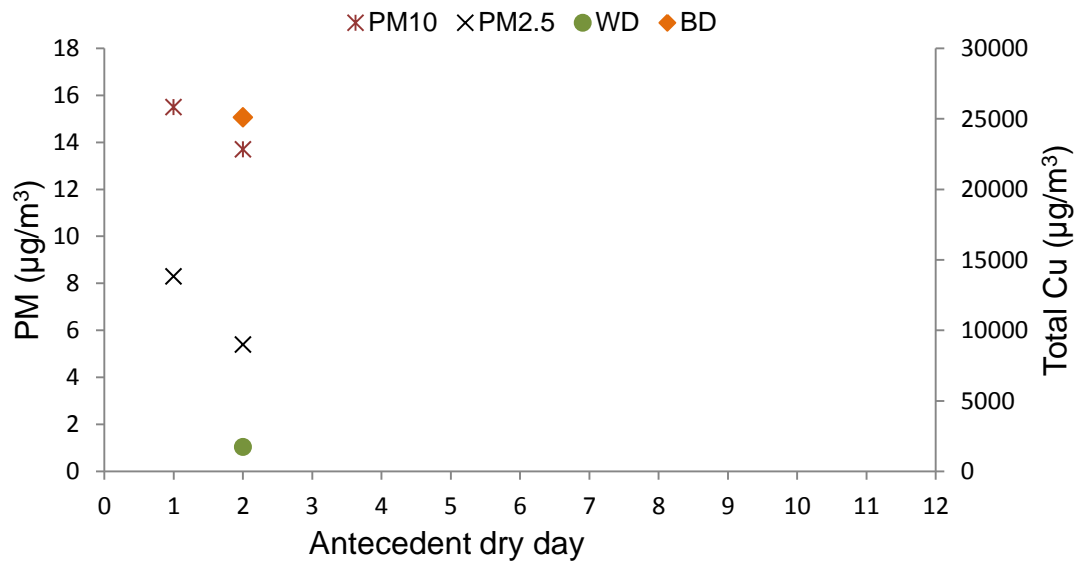
## Appendix C - The Effect of PM on Wet Deposition and Bulk Deposition Concentrations

The average daily concentrations of PM during the antecedent dry period was analysed against the concentration of total Cu in wet deposition (WD) and bulk deposition (BD). Details on each rain event analysed are exemplified in Table 7-2. As shown in the graphs, PM concentrations during the antecedent dry period does not have an effect on total Cu concentrations in WD and BD. This is principally due to the height of the PM monitoring set-up above ground, which only reflected PM concentrations in the lower troposphere. PM concentrations at higher altitudes, i.e. where cloud formation and rain-particle impaction occurs, were not represented. Additionally, concentrations of Cu in BD are likely to be influenced by other factors (e.g. wind speed) aside from ambient PM concentrations.

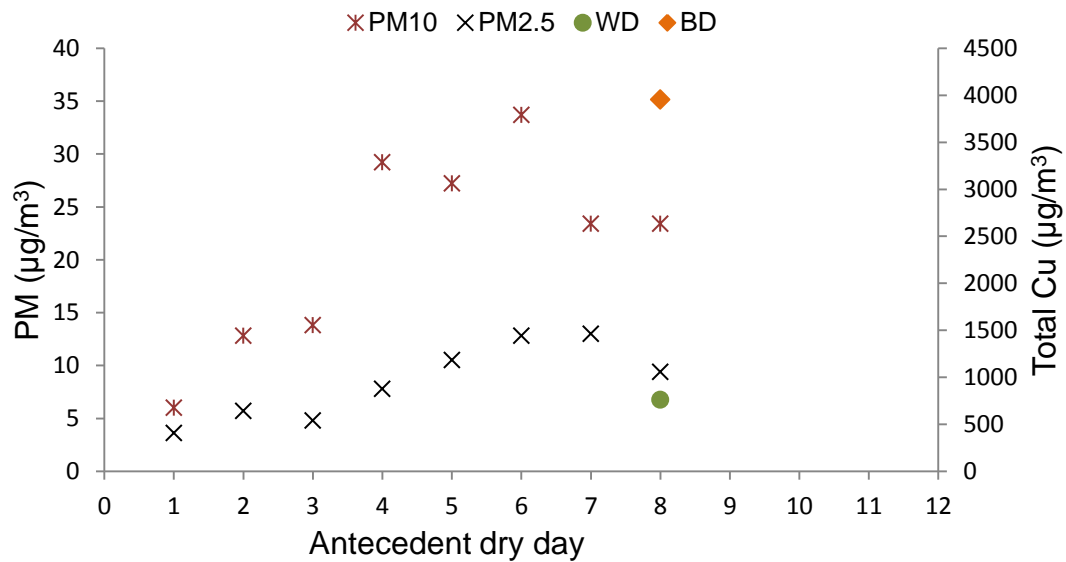
Rain event no. 1:



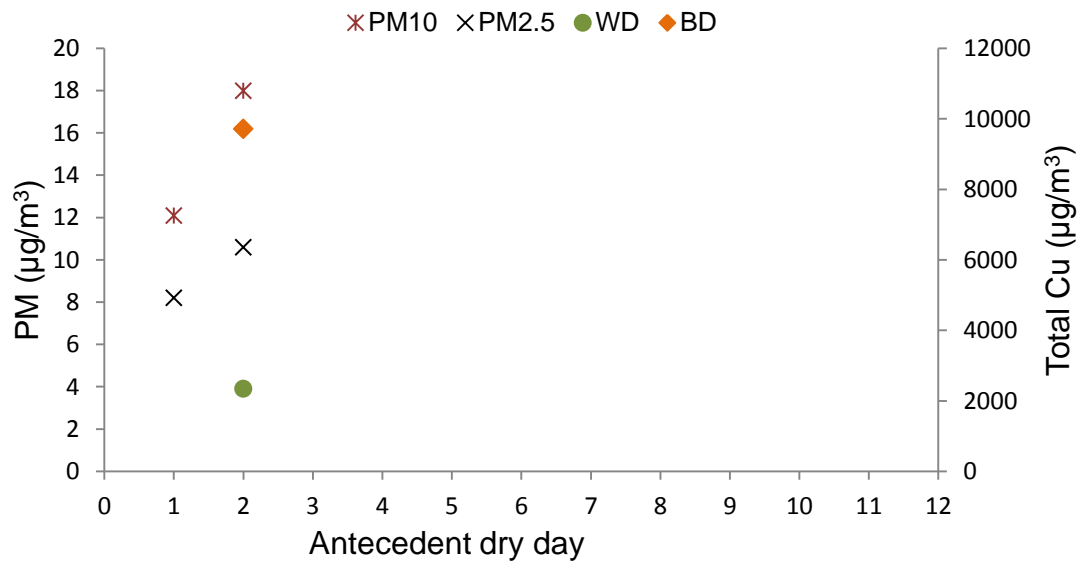
Rain event no. 2:



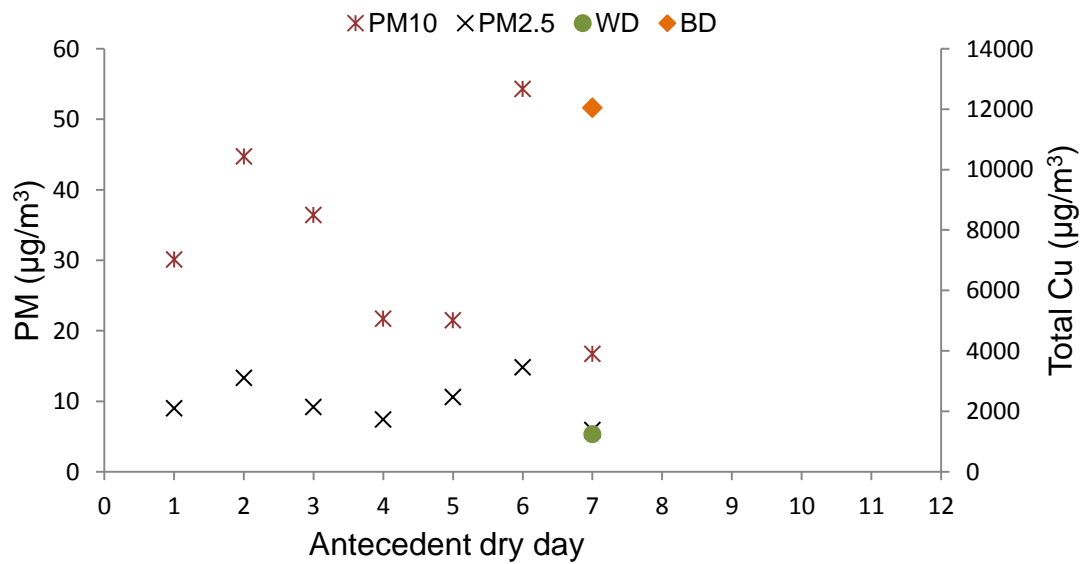
Rain event no. 3:



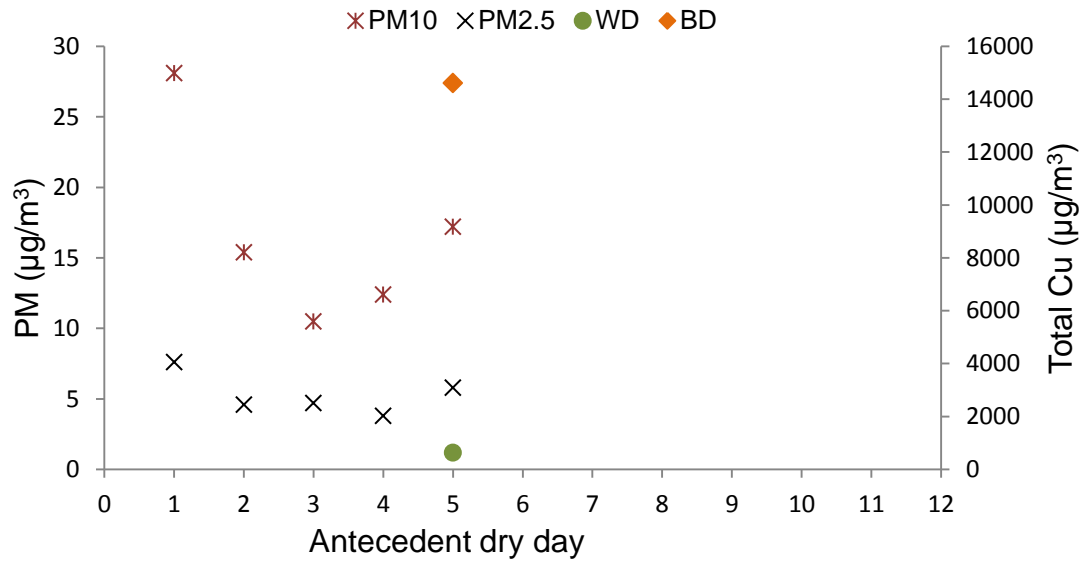
Rain event no. 4:



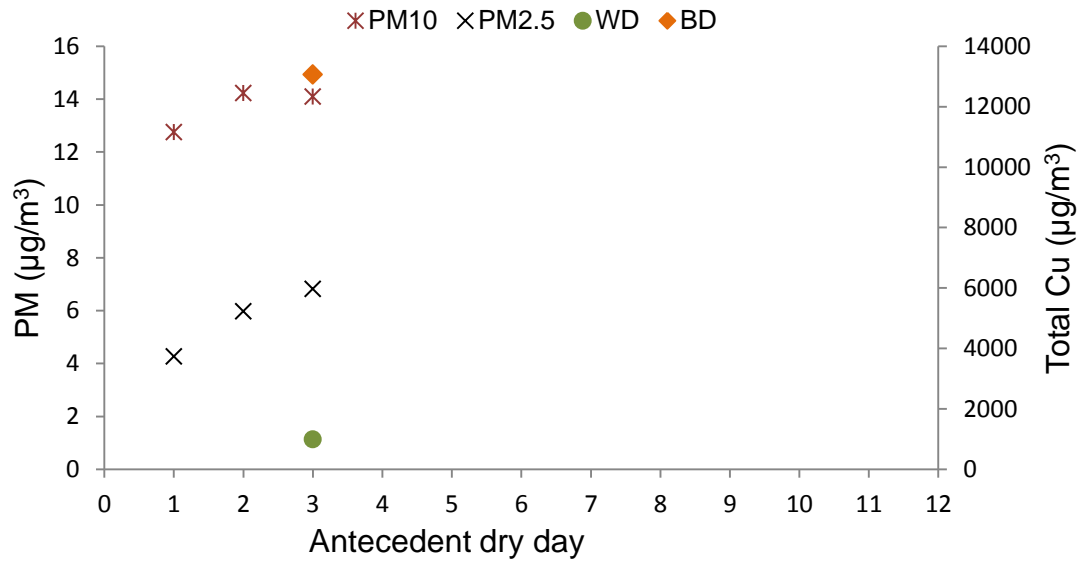
Rain event no. 5:



Rain event no. 6:



Rain event no. 7:



Rain event no. 8:

